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On the Theory of Reverberation

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ABSTRACT

This paper consists of four parts. In Part I two differential equations generally used for interpreting the reverberation and investigating the acoustic properties of building materials are discussed. In Part II the growth of sound in a single room when a source is sounding and its decay after the emission is stopped are studied, and a new formula for reverberation is obtained. In Part III the growth and decay of sound in two adjacent rooms are considered, and a new method of measuring the acoustic properties of building materials is proposed. In Part IV the method used by E. A. Eckhardt and V. L. Chrisler[1] for measuring the transmission of sound is discussed, and it is proved that the "reduction factor" defined by them is not a pure constant but a function depending generally on the rooms where the observations are made.

Part I

If e_1 be the sound energy incident on the surface of a body in a room, for instance, the wall, the ceiling, the floor, or a piece of furniture, and if e_2 be the part of e_1 which is preserved as sound energy in the room after the incidence, then we define the "coefficient of reduction" of the body by

$$r \equiv \frac{e_1 - e_2}{e_1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.1)$$

and assume that it is a constant depending on the nature of the body, but not on the incident energy e_1.

Let us consider the case where the room and the furniture are made

1 E. A. Eckhardt & V. L. Chrisler, B. S., Sci. Pap., **21**, 37 (1926).

of ν different kinds of material whose coefficients of reduction are $r_1, r_2, \ldots\ldots r_\nu$; and whose respective surface areas are $S_1, S_2, \ldots\ldots S_\nu$.

Let τ represent the mean value of the time-intervals between successive incidences of the sound energy on all the bodies in the room, and N the reciprocal of τ, *i. e.* the mean number of incidences in unit time.

Let us further assume that (A) the incidence of the sound energy in the room on the bodies takes place at equal intervals τ, and that (B) the incident amount of energy is divided proportionally among their respective surface areas.

When there is a source of sound in the room which can emit energy continuously at a constant rate ε, and if its emission is started, the sound energy in the room increases; and then if the emission is stopped, it begins to decrease. While if the emission is continued, the sound energy in the room tends to have a limiting value, and the state becomes steady.

Let $E_0^{(\infty)}$ be the sound energy in the room in this steady state. Then the part of $E_0^{(\infty)}$ which strikes the surface of the area S_i in an interval τ is $E_0^{(\infty)} \frac{S_i}{S}$, and consequently the loss of sound energy on that surface in an interval τ is $E_0^{(\infty)} \frac{S_i}{S} r_i$; where

$$S \equiv S_1 + S_2 + \ldots\ldots\ldots + S_\nu.$$

Therefore, the loss of sound energy from the room in an interval τ in the steady state is given by

$$\left.\begin{aligned} &\sum_{i=1}^{\nu} E_0^{(\infty)} \frac{S_i}{S} r_i = E_0^{(\infty)} R, \\ \text{where} \quad &R \equiv \frac{S_1 r_1 + S_2 r_2 + \ldots\ldots + S_\nu r_\nu}{S}; \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

and the sound energy lost in unit time is given by

$$\frac{E_0^{(\infty)} R}{\tau} = NRE_0^{(\infty)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.3)$$

Thus we see that in the steady state the loss of sound energy from the room in unit time is proportional to the sound energy in the room at that instant, and that its proportional constant is given by NR.

Let us now inquire into the loss which would take place when the sound energy in the room is in a state of increasing or of decreasing. Is it reasonable to assume that (a) in a state of increasing or of decreasing the loss of sound energy from the room in unit time is still

proportional to the sound energy in the room, and that (b) for the proportional constant the same proportional constant NR in the steady state may be used? In other words, if E', E be the sound energies in the room in the increasing and the decreasing states, are the two differential equations

$$\frac{dE'}{dt} = \varepsilon - NRE', \quad \text{(1.4)}$$

$$\frac{dE}{dt} = -NRE \quad \text{(1.5)}$$

satisfied by E' and E? The main object of Part I is to answer the above question.

If we assume these equations to be correct, we must have

$$E' = \frac{\varepsilon}{NR}\{1 - e^{-NRt}\}, \quad \text{(1.6)}$$

$$E = E_0 e^{-NRt}; \quad \text{(1.7)}$$

where E_0 is the sound energy when the emission is stopped, and t in (1.6) is measured from the instant when the sound from the source starts, and in (1.7) from the instant when it ceases to emit. These expressions are identical with those obtained by G. Jäger[1], E. A. Eckhardt[2], S. Nakamura[3], and E. Buckingham[4]. The relation (1.7) was already found by W. C. Sabine[5] before them.

Jäger also obtained the expression $N = \frac{cS}{4V}$; where c is the speed of sound and V the volume of the room, assuming that the sound energy is uniformly distributed throughout the room, both with regard to position and direction of propagation.

If we assume that the sound energy in the room after the source has ceased to emit sound is given by (1.7), then the sound energy in the room at t and $t + \tau$ are given by

$$E_t = E_0 e^{-NRt}, \quad E_{t+\tau} = E_0 e^{-NR(t+\tau)},$$

and therefore we have

$$E_{t+\tau} = E_t e^{-NR\tau} = E_t e^{-R}. \quad \text{(1.8)}$$

But the loss of sound energy from the room in the interval τ from t to

1 G. Jäger, Wiener Sitz. Ber., **120**, 613 (1911).
2 E. A. Eckhardt, Frank. Inst., J., **195**, 799 (1923).
3 S. Nakamura, 日本學術協會報告, **1**, 452 (1925).
4 E. Buckingham, B. S., Sci. Pap., **20**, 193 (1925).
5 W. C. Sabine, Collected Papers on Acoustics, pp. 34–37, 39.

$t + \tau$ must be E_tR, which is obtained by the same method as (1.2); and we must have

$$E_{t+\tau} = E_t - E_tR = E_t(1 - R) \quad \ldots\ldots (1.9)$$

The expressions (1.8) and (1.9) are incompatible unless R is zero. Hence we may conclude that (1.7) is not adaptable to the assumptions (A) and (B).

The inadaptability of (1.6) can similarly be inferred.

Now let us examine the differential equations (1.4) and (1.5). Let the curve in Fig. 1 show the decay of sound energy in the room after the emission is stopped. Let X_1M_1, Y_1N_1 represent the amounts of sound energy in the room at t and $t + \tau$ respectively, and X_1Y_1' the tangent to the curve at the point X_1, then we have

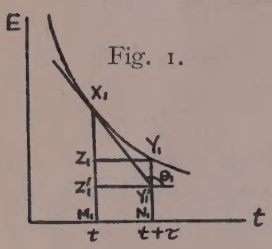


Fig. 1.

$$\begin{aligned} X_1Z_1 &= X_1M_1 - Y_1N_1 \\ &= E_t - E_{t+\tau} \\ &= E_tR \ . \end{aligned}$$

Dividing this by τ, we get

$$\frac{X_1Z_1}{\tau} = NE_tR$$

and this is exactly equal to the absolute value of the right hand side of (1.5). Namely we have

$$-NRE = -\frac{X_1Z_1}{\tau} \quad \ldots\ldots (1.10)$$

But the left hand side of (1.5) is

$$\frac{dE}{dt} = \tan\theta_1 = -\frac{X_1Z_1'}{Z_1'Y_1'} = -\frac{X_1Z_1'}{\tau}, \quad \ldots\ldots (1.11)$$

and X_1Z_1 is generally unequal to X_1Z_1'.

Next, let Fig. 2 show the growth of sound energy in the room, then we have

$$\begin{aligned} Y_2Z_2 &= Y_2N_2 - X_2M_2 \\ &= E_{t+\tau}' - E_t' \\ &= (\varepsilon\tau + E_t' - E_t'R) - E_t' \\ &= \varepsilon\tau - E_t'R, \end{aligned}$$

and

$$\frac{Y_2Z_2}{\tau} = \varepsilon - NRE_t' \quad \ldots\ldots (1.12)$$

That is, the right hand side of (1.4) is

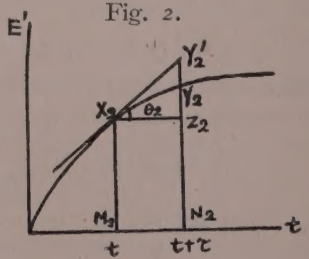


Fig. 2.

$\frac{Y_2Z_2}{\tau}$; but the left hand side of (1. 4) is

$$\frac{dE'}{dt} = \tan\theta_2 = \frac{Y_2'Z_2}{\tau}, \quad \text{.....(1. 13)}$$

and Y_2Z_2 is generally unequal to $Y_2' Z_2$.

Lastly, let N increase to infinity and R decrease to zero, while their product NR retains a finite constant value k. Then at the limit, the left hand sides of (1. 5) and (1. 4), or (1. 10) and (1. 12) become

$$-kE = -\lim_{\tau\to 0}\frac{X_1Z_1}{\tau} = \tan\theta_1 = \frac{dE}{dt},$$

$$\varepsilon - kE' \equiv \lim_{\tau\to 0}\frac{Y_2Z_2}{\tau} = \tan\theta_2 = \frac{dE'}{dt}$$

respectively, and the reduced forms of (1. 4) and (1. 5), i. e.,

$$\frac{dE'}{dt} = \varepsilon - kE',$$

$$\frac{dE}{dt} = -kE$$

are satisfied. The case where N tends to infinity and R to zero, while NR remains constant, will occur when the sound energy is lost by a certain continuous process, but not by such a discontinuous one as incidence.

When the sound energy in the room is discussed as a whole, the sum of all the fractions of sound energy which may be different from each other with regard to position or direction of propagation is considered. Since the sum is considered, the loss of sound energy from the room may appear to be continuous.

But, if the loss of some fractions of sound energy occur discontinuously by incidence, it is not reasonable to assume (1. 4) and (1. 5) to give the growth and decay of the sound energy in the room in a strict sense.

Part II.

If e_1 be the sound energy incident on the surface of a body in a room, and if e_2 be the part of e_1 which is preserved as sound energy in the room after the incidence, then let the quantity p given by

$$p \equiv \frac{e_2}{e_1} \quad \text{..... (2. 1)}$$

be called the "coefficient of preservation" of the sound by the body,

and assume that it is a constant depending on the nature of the body, but not on the incident energy e_1.

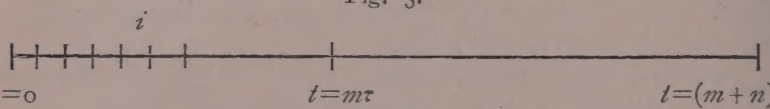
It should be noticed that the coefficient of preservation thus defined is different from the coefficient of reflection ordinarily used. Let e_1 be the incident sound energy and e_1', e_1'', e_1''' be the parts of e_1 which are reflected, transmitted, and dissipated by the body respectively. Then when the body struck by the sound wave is the wall of a room, $e_2=e_1'$ and the coefficient of preservation is the same as the coefficient of reflection; but if the body is a screen, $e_2=e_1'+e_1''$ and the coefficient of preservation is equal to the sum of the coefficient of reflection and that of transmission; while, if the screen last mentioned were used as a door, it is clear that we have $e_2=e_1'$.

Let τ represent the mean value of the time-intervals between successive incidences of the sound energy on all the bodies in the room, and ε the rate of emission, assumed constant, of a continuous sound source in the room.

Let the source start emitting in the previously soundless room at the time $t=0$ and cease to sound at the time $t=m\tau$, then let us obtain the sound energy in the room at the time $t=(m+n)\tau$, where m is a positive integer and n a positive integer or zero.

Divide the time-interval from $t=0$ to $t=m\tau$ into m equal short intervals and consider the sound energy emitted in the i-th short interval from the beginning, assuming that it strikes the bodies $(m+n-i)$ times by the time $t=(m+n)\tau$.

Fig. 3.



First, consider the simplest case where the coefficient of preservation p is constant for all incidences. An empty room made of a single material, with neither windows nor entrances is an example. In this case the sound energy under consideration will be reduced to

$$\varepsilon\tau p^{m+n-i} \quad \cdots\cdots (2.\ 2')$$

by $t=(m+n)\tau$ after $(m+n-i)$ incidences. Therefore, the sound energy E in the room at $t=(m+n)\tau$ is given by

$$E=\sum_{i=1}^{m}\varepsilon\tau p^{m+n-i}$$

$$=\varepsilon\tau\frac{1-p^m}{1-p}p^n \quad \cdots\cdots (2.\ 3')$$

Next, consider a more general case which would occur ordinarily; the room and the furniture are made of ν different kinds of material whose coefficients of preservation are $p_1, p_2, \ldots\ldots p_\nu$ and whose respective surface areas are $S_1, S_2, \ldots\ldots S_\nu$.

The sound energy $\varepsilon\tau$ emitted by the source in the i-th short interval is to strike the bodies once in the next interval. By assumption (B) we have

$$\varepsilon\tau \frac{S_1p_1+S_2p_2+\ldots\ldots+S_\nu p_\nu}{S}$$

as the reduced sound energy of $\varepsilon\tau$ at $t=(i+1)\tau$, where

$$S \equiv S_1 + S_2 + \ldots\ldots + S_\nu.$$

This sound energy will again be reduced to

$$\varepsilon\tau \left(\frac{S_1p_1+S_2p_2+\ldots\ldots+S_\nu p_\nu}{S}\right)^2$$

by $t=(i+2)\tau$, and to

$$\varepsilon\tau \left(\frac{S_1p_1+S_2p_2+\ldots\ldots+S_\nu p_\nu}{S}\right)^{m+n-i} \quad \ldots\ldots\ldots\ldots\ldots (2.2)$$

by $t=(m+n)\tau$. Hence the sound energy $E^{(m)}$ in the room at $t=(m+n)\tau$ is given by

$$\left.\begin{aligned} E^{(m)} &= \sum_{i=1}^{m} \varepsilon\tau \left(\frac{S_1p_1+S_2p_2+\ldots\ldots+S_\nu p_\nu}{S}\right)^{m+n-i} \\ &= \sum_{i=1}^{m} \varepsilon\tau\, P^{m+n-i} \\ &= \varepsilon\tau \frac{1-P^m}{1-P} P^n, \end{aligned}\right\} \quad \ldots\ldots\ldots (2.3)$$

where $$P \equiv \frac{S_1p_1+S_2p_2+\ldots\ldots+S_\nu p_\nu}{S} < 1.$$

The sound energy $E_0^{(m)}$ in the room, just when the source is stopped, is given by putting $n=0$ in (2.3), namely

$$E_0^{(m)} = \varepsilon\tau \frac{1-P^m}{1-P}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.4)$$

which is exactly the same as obtained by W. C. Sabine.[1]

The sound energy in the room, when the state becomes steady by prolonged use of the source, may be given by the limiting value of (2.4) when m tends to infinity, namely

1 W. C. Sabine, *op. cit.*, p. 44.

$$E_0^{(\infty)} = \varepsilon\tau \frac{1}{1-P} \quad \cdots\cdots (2.5)$$

This may be used to give the sound energy in the room even a few seconds after the source has started, when P is very small.

By (2. 3) and (2. 4), we have

$$E^{(m)} = E_0^{(m)} P^n \quad \cdots\cdots (2.3.1)$$

This expression or (2. 3) gives the sound energy in the room at the time of an integral multiple of τ, and not at any other time. But between n and t there exists a relation

$$t = (m+n)\tau.$$

Hence by puting

$$T \equiv t - m\tau,$$

we have

$$T = n\tau, \quad \text{or} \quad n = \frac{T}{\tau};$$

T represents the time measured from the instant when the source is stopped. Therefore we may write (2. 3. 1) as

$$E^{(m)} = E_0^{(m)} P^{\frac{T}{\tau}} \quad \cdots\cdots (2.3.2)$$

Now, let us assume that this represents the sound energy in the room at any instant T, which may be considered as a continuous variable.

Differentiating (2. 3. 2), we get

$$\frac{dE^{(m)}}{dt} = \frac{E_0^{(m)} \log P}{\tau} P^{\frac{T}{\tau}}$$

$$= -AE^{(m)},$$

where $$A \equiv -\frac{\log P}{\tau}. \quad \cdots\cdots (2.6)$$

It follows from this that the rate of decay of the sound energy in the room at any instant after the emission has ceased is proportional to the sound energy in the room at that instant. This was experimentally found by W. C. Sabine[1].

By a similar reasoning it may be assumed that the sound energy in the room at any instant when the source is sounding is given by the following continuous function of t:

1 W. C. Sabine, *op. cit.*, pp. 34–37.

$$E_0^{\left(\frac{t}{\tau}\right)} = \varepsilon\tau \frac{1-P^{\frac{t}{\tau}}}{1-P}, \qquad (2.4.1)$$

which is obtained from (2.4) by replacing m by $\frac{t}{\tau}$. Differentiating this, we get

$$\frac{dE_0^{\left(\frac{t}{\tau}\right)}}{dt} = -\varepsilon \frac{\log P}{1-P} P^{\frac{t}{\tau}} \qquad (2.7)$$

This gives the rate of growth of the sound energy in the room when the source is sounding.

Let D be the sound energy which is lost from the room in unit time in the steady state. Since in the steady state the loss of sound energy just balances the emission of the source, we must have

$$D = \varepsilon.$$

Hence, eliminating ε from this and (2.5), we get

$$\left.\begin{aligned} D &= \frac{1-P}{\tau} E_0^{(\infty)} \\ &= A^{(\infty)} E_0^{(\infty)}, \\ \text{where} \quad A^{(\infty)} &\equiv \frac{1-P}{\tau}. \end{aligned}\right\} \qquad (2.8)$$

Thus we see that in the steady state the loss of sound energy from the room in unit time is proportional to the sound energy in the room. This has been already obtained in Part I.

It is important to notice that A in (2.6) is not equal to $A^{(\infty)}$ in (2.8), but they are approximately equal only when P takes a value sufficiently near to 1; and in such a case (2.7) may be reduced to

$$\begin{aligned} \frac{dE_0^{\left(\frac{t}{\tau}\right)}}{dt} &\fallingdotseq \varepsilon P^{\frac{t}{\tau}} \\ &= \varepsilon - A^{(\infty)} E_0^{(\infty)} \qquad (2.7.1) \end{aligned}$$

Since $\frac{dE_0^{\left(\frac{t}{\tau}\right)}}{dt}$ is the rate of growth of the sound energy in the room and ε is the emission of sound energy from the source in unit time, $A^{(\infty)}E_0^{(\infty)}$ represents the rate of the loss of sound energy from the room. Hence, if P takes a value near to 1, the loss of sound energy from the room in unit time, when the source is sounding, is proportional to the sound energy in the room.

From these it follows that both when the sound energy in the room is increasing and decreasing, the loss of sound energy from the room in unit time may be approximately given by the produce of $A^{(\infty)}$

and the sound energy in the room, provided that P takes a value sufficiently near to 1.

Let T_2 represent the time-interval required to reduce the sound energy in the room, after the emission is stopped, to one half of its initial value, then from (2. 3. 2) we get

$$\frac{1}{2} E_0^{(m)} = E_0^{(m)} P^{\frac{T_2}{\tau}},$$

or
$$T_2 = \frac{\log 2}{-\log P} \tau \qquad \text{(2. 9)}$$

Thus we see that, if P remains constant, T_2 is proportional to τ. This shows the reason why the reverberation is strong in large rooms.

Let T_1 be the time when $E^{(m)}$ in (2. 3. 2) becomes a given value E_1, then we have

$$E_1 = E_0^{(m)} \left(\frac{S_1 p_1 + S_2 p_2 + \cdots\cdots + S_\nu p_\nu}{S} \right)^{\frac{T_1}{\tau}}.$$

Keeping E_1 and $E_0^{(m)}$ as fixed values, let S_1 be increased by $S_{1,2}$ and S_2 be decreased by $S_{1,2}$, then we have

$$E_1 = E_0^{(m)} \left\{ P + \frac{(p_1 - p_2) S_{1,2}}{S} \right\},$$

and, therefore,

$$\tau \log \frac{E_0^{(m)}}{E_1} = - T_1 \left\{ \log \left(1 + \frac{(p_1 - p_2) S_{1,2}}{PS} \right) + \log P \right\}.$$

If $\left| \frac{(p_1 - p_2) S_{1,2}}{PS} \right|$ be sufficiently small compared with 1, this may be written

$$\tau \log \frac{E_0^{(m)}}{E_1} \fallingdotseq T_1 \left\{ \frac{p_2 - p_1}{PS} S_{1,2} - \log P \right\} \qquad \text{(2. 10)}$$

This shows that there exists between $S_{1,2}$ and T_1 a relation of a rectangular hyperbola, which was found by W. C. Sabine[1] by experiments with cushions and open windows.

Part III

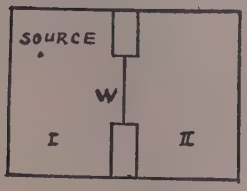
Let there be two adjacent rooms I and II which are in acoustic communication only through an incompletely soundproof panel W, which is set up as a part of the otherwise soundproof partition between the

1 W. C. Sabine, *op. cit.*, p. 20

rooms; and let the two rooms have the same acoustic properties, i. e. let P,S, and τ defined in Part II be the same for the two rooms.

Let us assume that the coefficient of transmission

Fig. 4.



$$q \equiv \frac{e_1''}{e_1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.\ 1)$$

where e_1 is the incident sound energy and e_1'' the part of the energy which passes through the body, is a constant independent of e_1. The coefficient of transmission q takes, of course, different values for different bodies.

Let a uniform and continuous sound source be started at the time $t=0$ to emit the energy at the rate ε in room I and the emission be stopped at the time $t=m\tau$. And let it be required to obtain the respective sound energies in the two rooms at the time $t=(m+n)\tau$, where m is a positive integer and n a positive integer or zero.

Dividing the time-interval from $t=0$ to $t=(m+n)\tau$ into $(m+n)$ equal short intervals, we shall calculate what amount of sound energy emitted by the source in the i-th $[i \leqq m]$ short interval would exist in room I at $t=(m+n)\tau$.

The sound energy $\varepsilon\tau$, which was emitted by the source in the i-th short interval and has never been in room II, reduces to

$$\varepsilon\tau\, P^{m+n-i}$$

by $t=(m+n)\tau$ after $(m+n-i)$ incidences in room I.

The sound energy, which went out into room II and came back again into room I passing through the panel twice, will undergo $(m+n-i-2)$ reflections in the time interval $(m+n-i)\tau$. So the part of sound energy $\varepsilon\tau$, which was emitted by the source in the i-th short interval and passed through the panel twice, reduces to

$$\varepsilon\tau \left(\frac{S_v}{S} q\right)^2 P^{m+n-i-2},$$

where S_v is the area of the panel W and q its coefficient of transmission. Hence

$$\varepsilon\tau_{m+n-i}\, C_2 \left(\frac{S_v}{S} q\right)^2 P^{m+n-i-2},$$

where ${}_{m+n-i}C_2$ shows the combination of 2 among $(m+n-i)$, gives the part of the sound energy which exists in room I at $t=(m+n)\tau$ having passed through the panel twice.

For the same reason,

$$\varepsilon\tau_{m+n-i}C_4\left(\frac{S_\nu}{S}q\right)^4 P^{m+n-i-4},\qquad \varepsilon\tau_{m+n-i}C_6\left(\frac{S_\nu}{S}q\right)^6 P^{m+n-i-6},\ \cdots\cdots$$

give the parts of energy which are present in room I at $t=(m+n)\tau$ having passed through the panel four times, six times, etc. respectively.

Therefore, the sound energy which was emitted by the source in the i-th short interval and exists in room I at $t=(m+n)\tau$ is

$$\varepsilon\tau\left\{P^{m+n-i}+{}_{m+n-i}C_2\left(\frac{S_\nu}{S}q\right)^2 P^{m+n-i-2}+{}_{m+n-i}C_4\left(\frac{S_\nu}{S}q\right)^4 P^{m+n-i-4}\right.$$
$$\left.+{}_{m+n-i}C_6\left(\frac{S_\nu}{S}q\right)^6 P^{m+n-i-6}+\cdots\right\},\ \cdots\cdots\cdots\cdots\ (3.2)$$

where ${}_\mu C_\lambda=0$ when $\mu<\lambda$.

Summing up (3.2) from $i=1$ to $i=m$, the sound energy $E_1^{(m)}$ in room I at $t=(m+n)\tau$ is given by

$$\left.\begin{aligned}E_1^{(m)}&=\varepsilon\tau\left\{\sum_{i=1}^{m}P^{m+n-i}+Q^2\sum_{i=1}^{m}{}_{m+n-i}C_2P^{m+n-i-2}\right.\\&\quad\left.+Q^4\sum_{i=1}^{m}{}_{m+n-i}C_4P^{m+n-i-4}+Q^6\sum_{i=1}^{m}{}_{m+n-i}C_6P^{m+n-i-6}+\cdots\cdots\right\}\\&=\varepsilon\tau\left\{\frac{1-P^m}{1-P}P^n+Q^2\sum_{j=n}^{m+n-1}{}_jC_2P^{j-2}+Q^4\sum_{j=n}^{m+n-1}{}_jC_4P^{j-4}\right.\\&\quad\left.+Q^6\sum_{j=n}^{m+n-1}{}_jC_6P^{j-6}+\cdots\cdots\right\},\end{aligned}\right\}\cdots\cdots\cdots\cdots\ (3.3)$$

where $Q\equiv\dfrac{S_\nu}{S}q.$

From this we can easily obtain the sound energy $E_{10}^{(m)}$ in room I when the emission of the sound energy is stopped, and the sound energy $E_{10}^{(\infty)}$ in room I when the source has sounded long enough to establish a steady state in both rooms as follows:

$$E_{10}^{(m)}=\varepsilon\tau\left\{\frac{1-P^m}{1-P}+Q^2\sum_{j=2}^{m-1}{}_jC_2P^{j-2}+Q^4\sum_{j=4}^{m-1}{}_jC_4P^{j-4}\right.$$
$$\left.+Q^6\sum_{j=6}^{m-1}{}_jC_6P^{j-6}+\cdots\cdots\right\},\ \cdots\cdots\cdots\cdots\cdots\ (3.4)$$

$$E_{10}^{(\infty)}=\varepsilon\tau\left\{\frac{1}{1-P}+\frac{Q^2}{(1-P)^3}+\frac{Q^4}{(1-P)^5}+\frac{Q^6}{(1-P)^7}\right.$$
$$\left.+\cdots\cdots\cdots\cdots\right\}$$
$$=\varepsilon\tau\frac{1-P}{(1-P)^2-Q^2}\ \cdots\cdots\cdots\cdots\cdots\cdots\ (3.5)$$

Similarly we obtain $E_{11}^{(m)}$, $E_{11\,0}^{(m)}$, and $E_{11\,0}^{(\infty)}$, the corresponding energy

amounts in room II, as follows:

$$E_{\mathrm{II}}^{(m)} = \varepsilon\tau\left\{Q\sum_{j=n}^{m+n-1} {}_jC_1\,P^{j-1} + Q^3\sum_{j=n}^{m+n-1} {}_jC_3\,P^{j-3} + Q^5\sum_{j=n}^{m+n-1} {}_jC_5P^{j-5} + \cdots\cdots\cdots\cdots\right\}, \quad (3.6)$$

$$E_{\mathrm{II}\,0}^{(m)} = \varepsilon\tau\left\{Q\sum_{j=1}^{m-1} {}_jC_1P^{j-1} + Q^3\sum_{j=3}^{m-1} {}_jC_3P^{j-3} + Q^5\sum_{j=5}^{m-1} {}_jC_5P^{j-5} + \cdots\cdots\cdots\cdots\right\}, \quad (3.7)$$

$$E_{\mathrm{II}\,0}^{(\infty)} = \varepsilon\tau\left\{\frac{Q}{(1-P)^2} + \frac{Q^3}{(1-P)^4} + \frac{Q^5}{(1-P)^6} + \cdots\cdots\right\}$$

$$= \varepsilon\tau\,\frac{Q}{(1-P)^2-Q^2} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3.8)$$

If the emission of the source be cut off after the sound energies in the two rooms have reached the steady values $E_{\mathrm{I}\,0}^{(\infty)}$, $E_{\mathrm{II}\,0}^{(\infty)}$ respectively, then the sound energies $E_{\mathrm{I}}^{(\infty)}$, $E_{\mathrm{II}}^{(\infty)}$ in the two rooms after the time $n\tau$ are given by

$$E_{\mathrm{I}}^{(\infty)} = \varepsilon\tau\,\frac{1-P}{(1-P)^2-Q^2}\left\{P^n + {}_nC_2Q^2P^{n-2} + {}_nC_4Q^4P^{n-4} + {}_nC_6Q^6P^{n-6} + \cdots\cdots\right\} + \varepsilon\tau\,\frac{Q}{(1-P)^2-Q^2}\left\{{}_nC_1QP^{n-1} + {}_nC_3Q^3P^{n-3} + {}_nC_5Q^5P^{n-5} + \cdots\cdots\right\}, \quad \cdots\cdots\cdots (3.9)$$

$$E_{\mathrm{II}}^{(\infty)} = \varepsilon\tau\,\frac{Q}{(1-P)^2-Q^2}\left\{P^n + {}_nC_2Q^2P^{n-2} + {}_nC_4Q^4P^{n-4} + {}_nC_6Q^6P^{n-6} + \cdots\cdots\right\} + \varepsilon\tau\,\frac{1-P}{(1-P)^2-Q^2}\left\{{}_nC_1QP^{n-1} + {}_nC_3Q^3P^{n-3} + {}_nC_5Q^5P^{n-5} + \cdots\cdots\right\}, \quad \cdots\cdots (3.10)$$

which are obtained by the same method as (3. 3), (3. 6).

If Q be so small that we may neglect the terms containing its higher powers, we get

$$E_{\mathrm{I}}^{(\infty)} \fallingdotseq \varepsilon\tau\,\frac{P^n}{1-P}, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3.9.1)$$

$$E_{\mathrm{II}}^{(\infty)} \fallingdotseq \varepsilon\tau\,\frac{\{P+n(1-P)\}P^{n-1}}{(1-P)^2}\,Q \quad \cdots\cdots\cdots (3.10.1)$$

In these expressions n denotes a positive integer or zero, but, by the same reasoning as we obtained (2. 3. 2) and (2. 4. 1), it may be

assumed that (3. 9. 1) and (3. 10. 1) are transformed into the following continuous functions of T:

$$E_{\mathrm{I}}^{(\infty)} = \varepsilon\tau \frac{P^{\frac{T}{\tau}}}{1-P}, \quad \cdots\cdots (3.\ 9.\ 2)$$

$$E_{\mathrm{II}}^{(\infty)} = \varepsilon\tau \frac{\left\{P+\frac{T}{\tau}(1-P)\right\}^{\frac{T}{\tau}-1}}{(1-P)^2} Q \quad \cdots\cdots (3.\ 10.2)$$

The decay of sound energy in two adjacent rooms was studied by E. Buckingham[1] and A. H. Davis[2] on the assumption that the sound energy in each room was uniformly distributed throughout the room, both with regard to position and direction.

We shall now propose a method of measuring the coefficients of preservation and transmission using two adjacent rooms.

Keeping P in (3. 5) as a fixed value, let Q become zero and let $E_0^{(\infty)}$ denote the value of $E_{\mathrm{I}\,0}^{(\infty)}$ in this case, then we get

$$E_0^{(\infty)} = \varepsilon\tau \frac{1}{1-P}, \quad \cdots\cdots (3.\ 11)$$

which is identical with (2. 5).

From (3. 5), (3. 8) we get

$$\frac{E_{\mathrm{I}\,0}^{(\infty)}}{E_{\mathrm{II}\,0}^{(\infty)}} = \frac{1-P}{Q}, \quad \cdots\cdots (3.\ 12)$$

and

$$\sqrt{\left\{E_{\mathrm{I}\,0}^{(\infty)}\right\}^2 - \left\{E_{\mathrm{II}\,0}^{(\infty)}\right\}^2} = \varepsilon\tau ; \quad \cdots\cdots (3.\ 13)$$

from (3. 11), (3. 13)

$$1 - P = \frac{\sqrt{\left\{E_{\mathrm{I}\,0}^{(\infty)}\right\}^2 - \left\{E_{\mathrm{II}\,0}^{(\infty)}\right\}^2}}{E_0^{(\infty)}} \equiv k ; \quad \cdots\cdots (3.\ 14)$$

and from (3. 12), (3. 14)

$$Q = k \frac{E_{\mathrm{II}\,0}^{(\infty)}}{E_{\mathrm{I}\,0}^{(\infty)}} \quad \cdots\cdots (3.\ 15)$$

Since $E_{\mathrm{I}\,0}^{(\infty)}$, $E_{\mathrm{II}\,0}^{(\infty)}$, and $E_0^{(\infty)}$ are all values in steady states, they and their ratios are measurable quantities; and, therefore, if they or their ratios are measured, P and Q may be obtained by (3. 14), (3. 15).

Let S_1 in each room be increased by $S_{1,2}$ and S_2 be decreased by $S_{1,2}$, then we get

1 E. Buckingham, *loc. cit.*

2 A. H. Davis, Phil. Mag., **50**, 75 (1925).

$$1 - P - \frac{(p_1 - p_2)S_{1,2}}{S} \equiv k'.$$

k' can be measured by the same method as k. Eliminating $1-P$ from this and (3. 14), we get

$$\frac{(p_1 - p_2)S_{1,2}}{S} = k' - k,$$

or

$$p_1 - p_2 = (k' - k)\frac{S}{S_{1,2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.16)$$

If either p_1 or p_2 is known, the other may be obtained by (3. 16). If S_2 is the area of an open window, and if its coefficient of preservation is assumed to be zero, (3. 16) becomes

$$p_1 = (k' - k)\frac{S}{S_{1,2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.17)$$

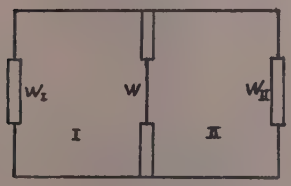
From (3. 15) we get

$$q = \frac{S}{S_v}Q = k\frac{S}{S_v}\frac{E_{\mathrm{II}\,0}^{(\infty)}}{E_{\mathrm{I}\,0}^{(\infty)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.18)$$

The coefficient of preservation and that of transmission may be obtained by (3. 17) and (3. 18).

In the course of this experiment it is necessary to make Q become zero without changing the value of P. This will be done, if the windows of room II are all opened, so that the sound energy may pass through the panel from room I to room II, but not back from room II to room I; or if a substance whose coefficient of preservation is very small is placed near the panel W in room II. There is another method. The rooms I and II are each provided with soundproof windows W_{I} and W_{II} as shown in Fig. 5, which have the same areas as W. After the values of $E_{\mathrm{I}\,0}^{(\infty)}$, $E_{\mathrm{II}\,0}^{(\infty)}$ have been obtained we measure $E_0^{(\infty)}$ by interchanging the material of the window W with that of W_{I}.

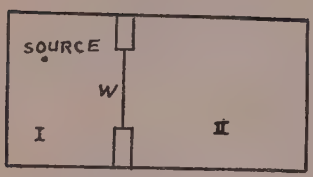
Fig. 5.



Part IV

Let there be two adjacent rooms I and II which are in acoustic communication only through a window W built in the partition between the rooms. Let F, H represent the respective average intensities in the

Fig. 6.



two rooms, with the window open when a uniform and continuous source in room I has sounded long enough to establish a steady state in both rooms. If an incompletely soundproof panel is fitted in the window W, the value of F is increased, say, to $F+f$, and that of H decreased, say, to $H-h$. If the average intensity were $F+f$ in room I with the window open, the average intensity in room II would be $H\frac{F+f}{F}$. Here we see that the average intensity in room II is reduced by the panel from $H\frac{F+f}{F}$ to $H-h$. E. A. Eckhardt and V. L. Chrisler[1] called the ratio of $H-h$ to $H\frac{F+f}{F}$, or

$$\frac{H-h}{H}\,\frac{F}{F+f} \qquad \text{..... (4. 1)}$$

the "reduction factor" of the panel and they observed this value for many kinds of building material.

Is the "reduction factor" which is defined by E. A. Eckhardt and V. L. Chrisler a constant depending only on the panel, but not on the rooms where the observations are made? In order to denote an acoustic property of the panel by the "reduction factor," it is necessary that the "reduction factor" be such a constant. The object of Part IV is to examine whether it is such a constant or not, under the same assumption as we have made before.

Let τ_{I}, P_{I}, Q_{I}, and τ_{II}, P_{II}, Q_{II} be the values of τ, P, Q for rooms I and II.

If E_{I}, E_{II} be the sound energies in the two rooms with the panel in place in the steady state, then the sound energies lost in unit time from room I and room II are

$$\frac{E_{\mathrm{I}}(1-P_{\mathrm{I}})}{\tau_{\mathrm{I}}}, \quad \frac{E_{\mathrm{II}}(1-P_{\mathrm{II}})}{\tau_{\mathrm{II}}}$$

respectively; and the sound energy received in unit time by room I from room II through the panel and that received by room II from room I are

$$\frac{E_{\mathrm{II}}Q_{\mathrm{II}}}{\tau_{\mathrm{II}}}, \quad \frac{E_{\mathrm{I}}Q_{\mathrm{I}}}{\tau_{\mathrm{I}}}.$$

Since the state is steady in both rooms, we must have the following two

1 E. A. Eckhardt & V. L. Chrisler, *loc. cit.*

equations :

$$\frac{E_{\mathrm{I}}(1-P_{\mathrm{I}})}{\tau_{\mathrm{I}}} = \varepsilon + \frac{E_{\mathrm{II}}Q_{\mathrm{II}}}{\tau_{\mathrm{II}}},$$

$$\frac{E_{\mathrm{II}}(1-P_{\mathrm{II}})}{\tau_{\mathrm{II}}} = \frac{E_{\mathrm{I}}Q_{\mathrm{I}}}{\tau_{\mathrm{I}}},$$

where ε is the rate of emission of the source. Solving these equations, we get

$$E_{\mathrm{I}} = \frac{\varepsilon\tau_{\mathrm{I}}(1-P_{\mathrm{II}})}{(1-P_{\mathrm{I}})(1-P_{\mathrm{II}})-Q_{\mathrm{I}}Q_{\mathrm{II}}}, \quad \ldots\ldots\ldots\ldots\ldots \quad (4.\,2)$$

$$E_{\mathrm{II}} = \frac{\varepsilon\tau_{\mathrm{II}}Q_{\mathrm{I}}}{(1-P_{\mathrm{I}})(1-P_{\mathrm{II}})-Q_{\mathrm{I}}Q_{\mathrm{II}}}. \quad \ldots\ldots\ldots\ldots\ldots \quad (4.\,3)$$

These expressions give the sound energies in rooms I and II with the panel in place. (4. 2) and (4. 3) are the generalized forms of (3. 5) and (3. 8).

Next, let E'_{I}, E'_{II} be the sound energies in rooms I and II with the window open; and P'_{I}, Q'_{I}, P'_{II}, Q'_{II} be the values of P_{I}, Q_{I}, P_{II}, Q_{II} in this case. Then we have

$$E'_{\mathrm{I}} = \frac{\varepsilon'\tau_{\mathrm{I}}(1-P'_{\mathrm{II}})}{(1-P'_{\mathrm{I}})(1-P'_{\mathrm{II}})-Q'_{\mathrm{I}}Q'_{\mathrm{II}}}, \quad \ldots\ldots\ldots\ldots\ldots \quad (4.\,4)$$

$$E'_{\mathrm{II}} = \frac{\varepsilon'\tau_{\mathrm{II}}Q'_{\mathrm{I}}}{(1-P'_{\mathrm{I}})(1-P'_{\mathrm{II}})-Q'_{\mathrm{I}}Q'_{\mathrm{II}}}, \quad \ldots\ldots\ldots\ldots\ldots \quad (4.\,5)$$

as the expressions corresponding to (4. 2), (4. 3); where ε' is the rate of emission of the source which is adjusted to satisfy the condition

$$E_{\mathrm{I}} = E'_{\mathrm{I}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.\,6)$$

It is clear that the "reduction factor" defined by E. A. Eckhardt and V. L. Chrisler is equal to $\frac{E_{\mathrm{II}}}{E'_{\mathrm{II}}}$.

From (4. 3), (4. 5) we get

$$\frac{E_{\mathrm{II}}}{E'_{\mathrm{II}}} = \frac{\varepsilon}{\varepsilon'}\,\frac{(1-P'_{\mathrm{I}})(1-P'_{\mathrm{II}})-Q'_{\mathrm{I}}Q'_{\mathrm{II}}}{(1-P_{\mathrm{I}})(1-P_{\mathrm{II}})-Q_{\mathrm{I}}Q_{\mathrm{II}}}\,\frac{Q_{\mathrm{I}}}{Q'_{\mathrm{II}}}; \quad \ldots \quad (4.\,7)$$

and from (4. 2), (4. 4), (4. 6)

$$\frac{\varepsilon(1-P_{\mathrm{II}})}{(1-P_{\mathrm{I}})(1-P_{\mathrm{II}})-Q_{\mathrm{I}}Q_{\mathrm{II}}} = \frac{\varepsilon'(1-P'_{\mathrm{II}})}{(1-P'_{\mathrm{I}})(1-P'_{\mathrm{II}})-Q'_{\mathrm{I}}Q'_{\mathrm{II}}},$$

or

$$\frac{\varepsilon}{\varepsilon'}\,\frac{(1-P'_{\mathrm{I}})(1-P'_{\mathrm{II}})-Q'_{\mathrm{I}}Q'_{\mathrm{II}}}{(1-P_{\mathrm{I}})(1-P_{\mathrm{II}})-Q_{\mathrm{I}}Q_{\mathrm{II}}} = \frac{1-P'_{\mathrm{II}}}{1-P_{\mathrm{II}}}.$$

Substituting this in (4. 7) we get

$$\frac{E_{II}}{E'_{II}} = \frac{1-P'_{II}}{1-P_{II}} \frac{Q_I}{Q'_I} \quad \cdots\cdots (4.8)$$

For the values of $1-P_{II}$ and Q_I we have

$$1 - P_{II} = \frac{(1-\phi_1)S_1 + \cdots\cdots + (1-\phi_{\nu-1})S_{\nu-1} + (1-\phi_\nu)S_\nu}{S_{II}}, \quad \cdots\cdots (4.9)$$

$$Q_I = \frac{S_\nu}{S_I} q; \quad \cdots\cdots (4.10)$$

where S_I, S_{II} are the surface areas of rooms I and II, and ϕ_ν, q the coefficients of preservation and of transmission of the panel. Since for the open window we may assume that its coefficients of preservation and of transmission are zero and unity respectively, we have

$$1 - P'_{II} = \frac{(1-\phi_1)S_1 + \cdots\cdots + (1-\phi_{\nu-1})S_{\nu-1} + S_\nu}{S_{II}}, \quad \cdots\cdots (4.11)$$

$$Q'_I = \frac{S_\nu}{S_I} \quad \cdots\cdots (4.12)$$

Comparing (4. 11) with (4. 9) we get

$$1 - P'_{II} = (1 - P_{II}) + \phi_\nu \frac{S_\nu}{S_{II}} \quad \cdots\cdots (4.13)$$

Substituting (4. 10), (4. 12) into the expression (4. 8) we get

$$\frac{E_{II}}{E'_{II}} = \frac{1-P'_{II}}{1-P_{II}} q \quad \cdots\cdots (4.13)$$

If $1-P_{II}$ were equal to $1-P'_{II}$, the "reduction factor" is the same as the coefficient of transmission. But, as (4. 13) shows, $1-P'_{II}$ differs from $1-P_{II}$ by

$$\phi_\nu \frac{S_\nu}{S_{II}};$$

and since P_{II} and ϕ_ν will often take values near to 1, we can in general not neglect this difference compared with $1-P_{II}$.

Therefore, we may conclude that the "reduction factor" defined by E. A. Eckhardt and V. L. Chrisler depends generally on the values of P'_{II} and $\frac{S_\nu}{S_{II}}$, *i. e.* on the rooms where the observations are made.

The writer wishes to express his sincere thanks to Professor K. Tamaki by whose suggestion this investigation was undertaken.

On the Brinell Hardness of the Ternary Alloys consisting of Copper, Zinc and Aluminium as an α-solid solution.

By

Hiroshi Kawai.

(Received January 24, 1928)

Introduction.

The hardness of the binary alloys has hitherto been studied by several workers; the results may be summarised as follows:—

1 The hardness increases with the addition of one component to the other, when both are perectly soluble, showing a maximum when the composition is just in the proportion of the atomic weights;[1]

2 When both metals are not completely soluble, the maximum lies in the field of the solid solution, as long as the solubility is relatively large; but with a less solubility, the hardness rises to the saturation point, there cutting the curve as its end value;[2]

3 When one component is soluble in the other, the hardness becomes greater in proportion to the decreasing rate of solubility.[3]

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1 Kurnakow and Zemczuzny, Journ. Russ. Phys.-Chem. Soc., 1908, vol. xl, 1067–1104; Harris, Journ. Inst. Metals, 1922, No. 2, 328.

2 Turner and Murry. Journ. Inst. Metals, 1909, No. 2, 137; Johnson, Journ. Inst. Metals, 1918, No. 2, 233; Haughton, Journ. Inst. Metals, 1918, No. 2, 243; Harris, Journ. Inst. Metals, 1922, No. 2, 330.

3 Norbury, Journ. Inst. Metals, 1923, No. 1, 423; Jeffries and Archer, Sci. Metals, 1924, 257.

It seems, however, that no papers on the ternary alloys as solid solutions have yet been published, so that the present writer has taken up the subject with respect to the alloys consisting of copper, zinc and aluminium as an α-solid solution.

Experiment.

The copper, zinc and aluminium used as materials were of the best quality that could be obtained in the market. They wery melted together in the required proportions, cast, annealed for 2–3 hours at 650°, cut parallel in 2 opposite surfaces and well polished.

The hardness test was made thrice and the mean value taken for each specimen, using a 2 mm ball with a load of 40 kg for one minute, so that the ratio of the load to the diameter of the ball should be 10.[1]

All the results of the experiments are tabulated in Table I, while in Table II, the hardness is given at the position denoted by the weight percentage of zinc as abscissa and that of aluminium as ordinate. The asterisks in the latter Table refer to the specimens containing the β-phase, the existence of which is obvious from the annexed microphotograms.

The microphotograms, Nos. 11, 19, 27, 34, 40, 44, 47 and 49 represent the specimens consisting of the β-phase intermixed with the α, while Nos. 10, 18, 26, 32, 39, 43 and 46 are those cut from the α-field very near to the boundary line.

The curve, Fig. 1, shows the variation of the Brinell hardness due to the addition of aluminium to the α-solid solution consisting of Cu and Al. The curve, Fig. 2, shows the hardness variation due to the addition of aluminium to the α-soild solution consisting of Cu with 5% Zn. The curves, Figs. 3, 4, 5, 6 and 7 show respectively the variation due to the addition of aluminium to the Cu–alloys consisting of 10, 15, 20, 25 and 30% Zn,

As may be seen from the curves, Figs. 1, 2, 3, 4 and 5, where the solubility–limits are relatively large, the maximum hardness appears within that limit, but from the curves, Figs. 6 and 7, where the solubility–limits are narrower, the hardness rises to the phase boundary, beyond which it still continues to rise in the β–field. When the maximum points in the α–field are connected as in Fig. 8, we obtain a smooth curve drawn in a dotted line, which indicates that the variation of the hardness by the addition of aluminium is continuous, the maximum

1 Brownson, Journ. Inst. Metals, 1923, No. 2, 69.

appearing at 15% Zn–alloy with 3% Al added.

Next, the same result was reached with the Cu–Al–alloys with zinc added. The curve, Fig. 9, shows the variation of the hardness with the increasing amount of zinc in the Cu–Zn-alloys, while the curves, Figs. 10, 11, 12, 13, 14, 15, 16 and 17 show respectively its variation due to the addition of zinc to the Cu–Al–alloys containing 1, 2, 3, 4, 5, 6, 7 and 8% Al. When the maximum points are connected as in Fig. 18, we get a curve drawn in a dotted line, which shows the maximum hardness lies in the alloy consisting of 15% Zn, 3% Al and 82% Cu.

Summary.

1 The variation of the hardness in the ternary alloys shows the same relation as with the binary alloys.

2 When the solubility–limits are relatively large, there exists a maximum in the field of the solid solution.

3 When the limits are relatively narrow, the hardness curve will continue to rise, till it reaches the boundary line.

4 Beyond the boundary line, the curve still continues to rise gradually or very rapidly, as the case might determine.

Table I.

Diameter of ball: 2 mm. Load: 40 kg.

No.	Weight percent of components			Diameter of impression in mm	Brinell hardness
	Cu	Zn	Al		
1	100	—	—	1.108	38
2	99	—	1	1.095	39
3	98	—	2	1.070	41
4	97	—	3	1.025	45
5	96	—	4	0.985	49
6	95	—	5	0.950	53
7	94	—	6	0.950	53
8	93	—	7	0.924	56
9	92	—	8	0.950	53
10	91	—	9	0.968	51
11	90	—	10	0.893	60
12	95	5	—	1.035	44
13	94	5	1	1.005	47
14	93	5	2	0.975	50
15	92	5	3	0.958	52
16	91	5	4	0.934	55
17	90	5	5	0.923	56
18	89	5	6	0.933	55
19	88	5	7	0.867	65
20	87	5	8	0.708	99
21	90	10	—	1.025	45
22	89	10	1	0.995	48
23	88	10	2	0.957	52
24	87	10	3	0.950	53
25	86	10	4	0.897	59
26	85	10	5	0.950	53
27	84	10	6	0.792	77
28	83	10	7	0.720	95
29	85	15	—	0.995	48
30	84	15	1	0.950	53
31	83	15	2	0.893	60
32	82	15	3	0.840	66

33	81	15	4	0·942	54
34	80	15	5	0·772	82
35	79	15	6	0·650	117
36	80	20	—	0·950	53
37	79	20	1	0·910	58
38	78	20	2	0·892	60
39	77	20	3	0·925	56
40	76	20	4	0·840	69
41	75	20	5	0·660	114
42	75	25	—	0·975	50
43	74	25	1	0·918	57
44	73	25	2	0·864	65
45	72	25	3	0·704	99
46	70	30	—	1·024	45
47	69	30	1	0·892	60
48	68	30	2	0·691	104
49	65	35	—	1·015	46

Table II.

Weight per-cent of aluminium.

Weight per cent of zinc.	0	1	2	3	4	5	6	7	8	9	10
0	38	39	41	45	49	53	53	56	53	51	60*
5	44	47	50	52	55	56	55	65*	99*		
10	45	48	52	53	59	53	77*	95*			
15	48	53	60	69	54	82*	117*				
20	53	58	60	56	69*	114*					
25	50	57	65*	99*							
30	45	60*	104*								
35	46*										

Fig. 1.
Brinell hardness of copper-aluminium alloys.

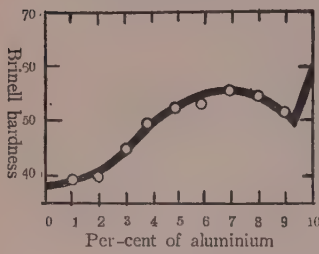


Fig. 2.
Brinell hardness of copper-zinc-aluminium Alloys, containing 5% zinc:

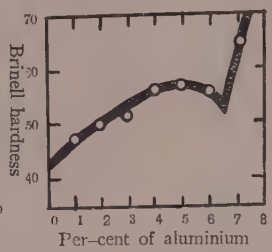


Fig. 3.
Brinell hardness of copper-zinc-aluminium alloys, containing 10% zinc.

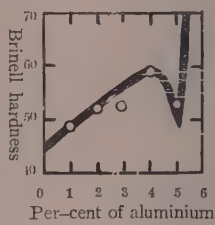


Fig. 4.
Brinell hardness of copper-zinc-aluminium alloys containing 15% zinc.

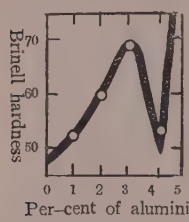


Fig. 5.
Brinell hardness of copper-zinc-aluminivm alloys containing 25% zinc.

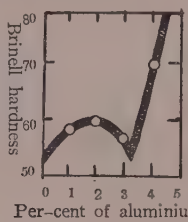


Fig. 6.
Brinell hardness of copper-zinc-aluminium alloys containing 25% zinc.

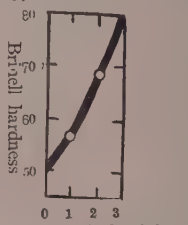


Fig. 7.
Brinell hardness of copper-zinc-aluminium alloys containing 30% zinc.

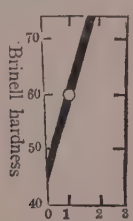


Fig. 8.
Brinell hardness of copper-zinc aluminium alloys.

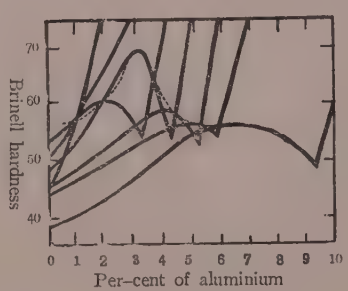


Fig. 9.

Brinell hardness of copper-zinc alloys.

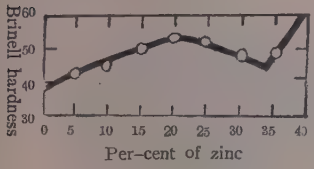


Fig. 10.

Brinell hardness of copper-zinc-aluminium alloys, containing 1% aluminium.

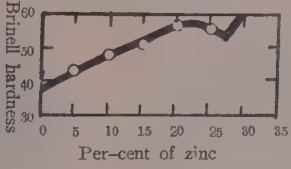


Fig. 11.

Brinell hardness of copper-zinc-aluminium alloys, containing 2% aluminium.

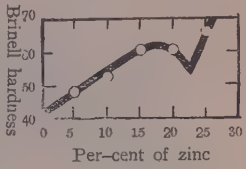


Fig. 12.

Brinell hardness of copper-zinc-aluminium alloys, containing 3% aluminium.

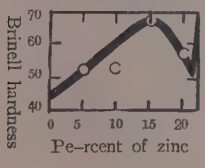


Fig. 13.

Brinell hardness of copper-zinc-aluminium alloys, containing 4% aluminium.

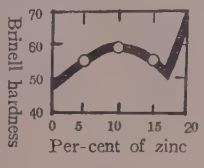


Fig. 14.

Brinell hardness of copper-zinc-aluminium alloys, contaning 5% aluminium.

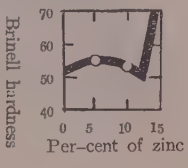


Fig. 15.

Brinell hardness of copper-zinc-aluminium alloys, containing 6% aluminium.

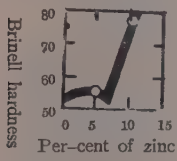


Fig. 16.

Brinell hardness of copper-zinc-aluminium alloys, containing 7% aluminium.

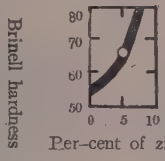


Fig. 17.

Brinell hardness of copper-zinc-aluminium alloys, containing 8% aluminium.

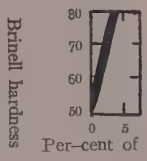
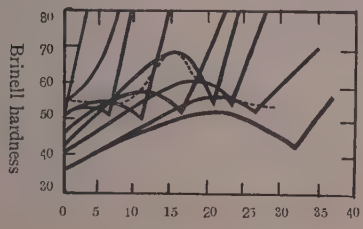
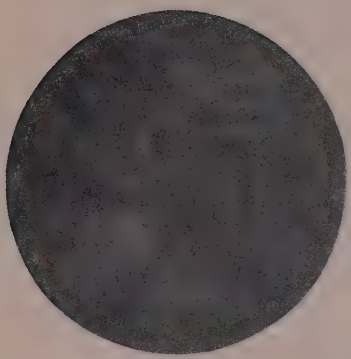


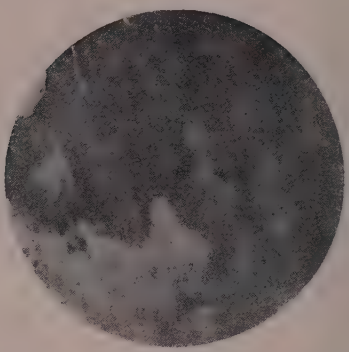
Fig. 18.

Brinell hardness of copper-zinc-aluminium alloys.

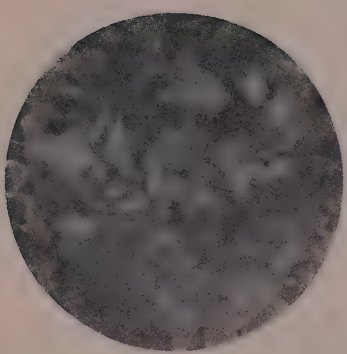




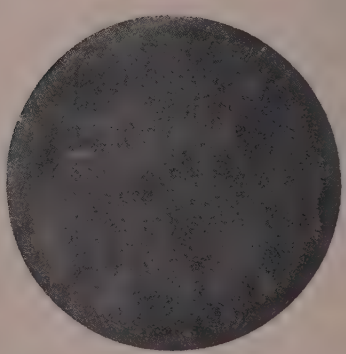
No. 11. Copper-zinc alloy, containing 10 % Zn, annealed for 2 hours at 650.°



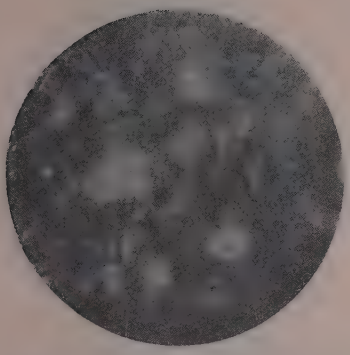
No. 16. Copper-zinc aluminium alloy, containing 5 % Zn and 7 % Al, annealed for 2 hours at 650.°



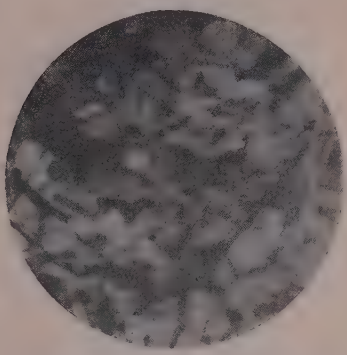
No. 27. Copper-zinc-aluminium alloy, containing 10 % Zn and 6 % Al, annealed for 2 hours at 650.°



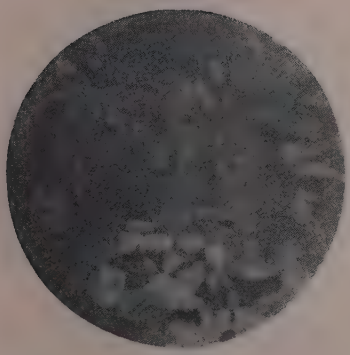
No. 34. Copper-zinc-aluminium alloy, containing 15 % Zn and 5 % Al, annealed for 2 hours at 650.°



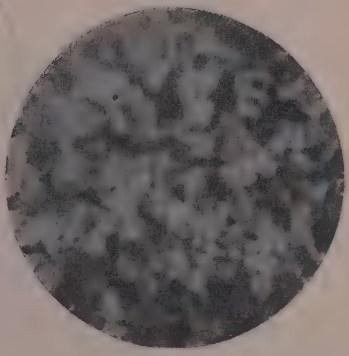
No. 40. Copper-zinc-aluminium alloy, containing 20 % Zn and 4 % Al, annealed for 2 hours at 650.°



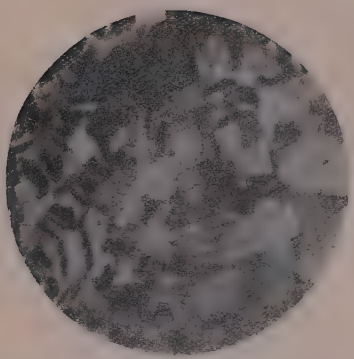
No. 44. Copper-zinc-aluminium alloy, containing 25% Zn and 3 % Al, annealed for 3 hours at 650.°



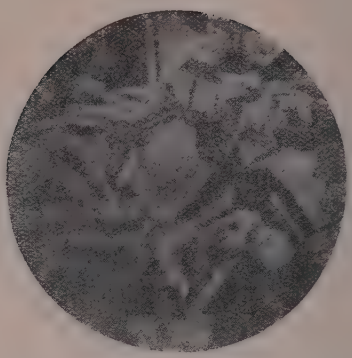
No. 47. Copper-zinc-aluminium alloy, containing 30 % Zn and 1 % Al, annealed for 3 hours at 650.°



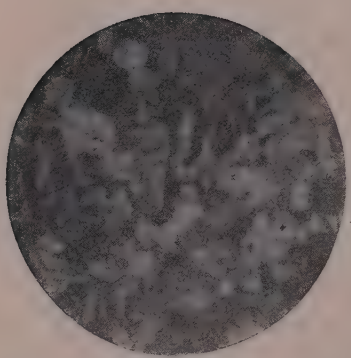
Ny. 49. Copper-zinc alloy, contaiuing 35 % Zn, annealed for 3 hours at 650.°



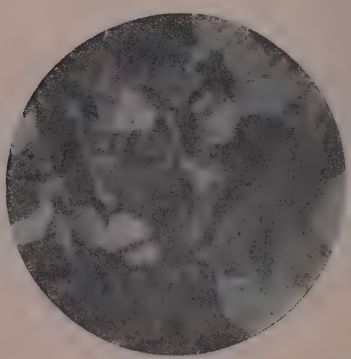
No. 10. Copper-aluminium alloy, containina 9 % Al, annealed for 2 hours at 650.°



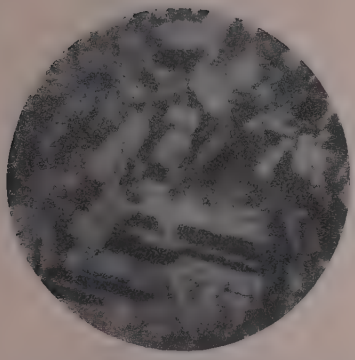
No. 18. Copper-zinc-aluminium alloy, containing 5% Zn and 6 % Al, annealed for 2 hours at 650.°



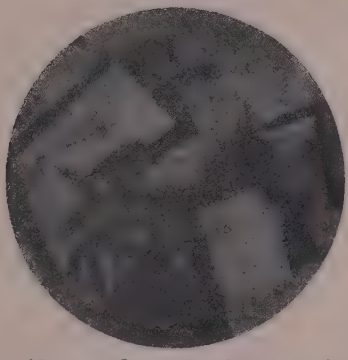
No. 26. Copper-zinc-aluminium alloy, containing 10 % Zn and 5 % Al, annealed for 2 hours at 650.°



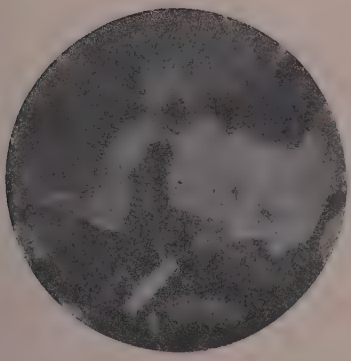
No. 32. Copper-zinc-aluminium alloy, containing 15 % Zn and 4 % Al, annealed for 2 hours at 650.°



No. 39. Copper-zinc-aluminium alloy, containing 20 % Zn and 3 % Al, annealed for 2 hours at 650.°



No. 43. Copper-zinc-aluminium alloy, containing 25 % Zn and 1 % Al, annealed for 3 hours at 650.°



No. 46. Copper-zinc alloy, containing 30 % Zn, annealed for 3 hours at 650.°

On the Measurements of the Vapour Pressures of Concentrated Aqueous Solutions of Potassium Iodide.

By

Noboru Furutani.

(Received January 27, 1928)

The vapour pressures of the aqueous solutions of various substances were measured at various concentrations by many investigators. But there are only a few examples of measurements for highly concentrated solutions, especially at high temperatures. As for the vapour pressures of the potassium iodide solutions, Tamman,[1] Dieterici[2] and Börsted[3] measured them only in dilute conditions and at temperatures below 100°C, so the writer carried out the measurements of the vapour pressures of the concentrated potassium iodide solutions at high temperatures with the special method[4] which is very convenient for this purpose, and the present paper gives the results of the experiments and some calculations derived from these results.

Samples and Method of Experiments.

The potassium iodide used was that of the Japanese Pharmacopoeia three times purified by recrystallisation. By the action of oxygen and carbon dioxide, potassium iodide easily sets free iodine in its aqueous solution. For this reason, the conductivity water, which was made as free as possible of dissolving air, was used as the solvent. The whole

1 Wied. Ann., **24**, 530 (1885); Mem. Acad. Pét., (7), **35** (1891).
2 Wied. Ann., **42**, 513 (1891).
3 Zs. physik. Chem., **82**, 633 (1913)
4 See the method of the determination of the vapour pressure of phosphorus by Smits and Bokhorst: Zs. physik. Chem., **91** 248, (1916).

apparatus used is shown in Fig. 1. S is the pressure indicator made of Pyrex glass, a more detailed construction of which can be seen from Fig. 2. This pressure indicator was connected with a metal tube at *g* in the following way: The glass tubing of the top of the indicator was first coated with platinum, and then on this platinum film copper was electrochemically plated, then this part was closely connected with a metal tube by soldering.

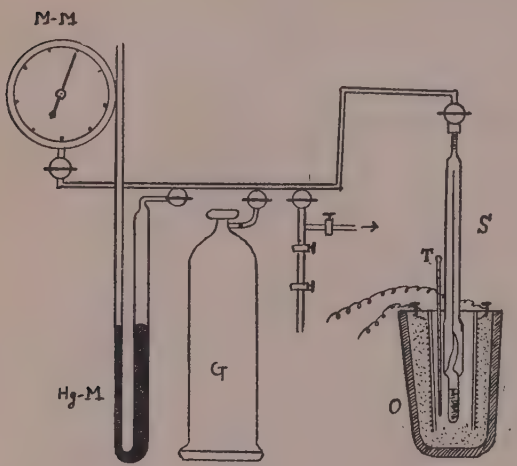


Fig. 1.

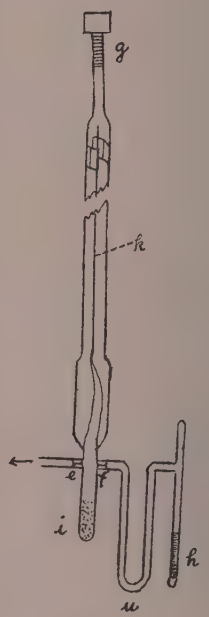


Fig. 2.

A weighed amount of purified potassium iodide was put into *i*, and the measured amount of solvent was poured into *h*. Now *h*, *u* and *i* were evacuated by means of a vacuum pump, while *u* was kept cool with liquid air. In this procedure, the water in *h* was distilled toward *u in vacuo*. After a sufficient vacuum was obtained, the connection between the pressure indicator and the vacuum pump was sealed at *e*. Then water was distilled again from *u* to *i*, and *h* and *u* were sealed off at *f*. Thus a solution of potassium iodide of a known concentration can be obtained in *i*.

The furnace used, which is represented by O in Fig. 1, was made

up of an iron tube, 5 cm. in inner diameter and 33 cm. in length, which was electrically heated by a nichrome wire, and this iron tube was kept in a large crucible filled with asbestos fibre. Through the regulation of current intensity it is able to keep the temperature constant for several minutes. All the connections can easily be seen from Fig. 1. G is the bomb of carbon dioxide which brings high pressure to the system of the apparatus, outside the spring of the indicator. Hg–M is a manometer of mercury for the measurement of pressures up to 3 atmospheres, and M–M is that of metal for higher pressures. The pressure of the solution in the enclosed part *i* at any desired temperature can be read indirectly on the scales of Hg–M and M–M by adjusting the pressure of the system of the measurement to fix always the pointer *k* at zero point.

Results of the Experiments.

The vapour pressures of the potassium iodide solutions of various concentrations were measured by the above-mentioned method at every interval of five degrees between 30°—200°C. Only the results obtained above 100° are shown in the following tables (from II to XI).

Table I

H_2O 100.00 g.
KI 0.00 g. $C = 13.05$

t° C.	p_o (atms)	$T\ln p_o$	CT	L/R
100	1	0.	4867·7	4868
105	1·19	65·8	4932·9	4867
110	1·41	131·6	4998·1	4866
115	1·67	199·0	5063·4	4865
120	1·96	264·5	5128·6	4864
125	2·29	329·8	5198·9	4864
130	2·67	396·8	5259·2	4862
135	3·09	460·4	5324·4	4864
140	3·57	525·7	5389·6	4864
145	4·10	589·9	5455·0	4865
150	4·69	653·8	5520·1	4866
155	5 36	718·7	5585·4	4867
160	6·10	783·1	5650·6	4868
165	6·92	847·4	5715·9	4869
170	7·82	911·3	5781·1	4870
175	8·81	975·0	5846·4	4871
180	9·89	1038·2	5911·7	4854
185	11·09	1102·2	5977·0	4875
190	12·39	1165·5	6042·1	4877
195	13·80	1228·6	6107·4	4879
200	15·34	1292·0	6172·6	4881

Table II

H_2O 86.86 g. KI 13.14 g. $\frac{N_1^*}{N_2} = 61.5$ C=12.87

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0.926	−28.7	4800.5	4829	0.926
105	1.17	59.4	4864.9	4806	0.983
110	1.37	120.6	4929.2	4809	0.972
115	1.60	182.4	4993.6	4811	0.958
120	1.87	246.0	5057.9	4812	0.954
125	2.22	317.5	5122.2	4805	0.969
130	2.55	378.2	5186.6	4808	0.955
135	2.95	441.5	5250.9	4810	0.955
140	3.45	511.5	5315.3	4804	0.966
145	3.92	571.1	5379.7	4809	0.956
150	4.49	635.4	5444.0	4809	0.957
155	5.14	700.8	5508.4	4801	0.959
160	5.85	764.3	5572.7	4809	09.59
165	6.62	828.0	5637.1	4809	0.957
170	7.40	886.8	5701.5	4815	0.946
175	8.34	950.4	5765.8	4815	0.947
180	9.45	1017.6	5830.1	4813	0.956
185	10.50	1077.1	5894.5	4817	0.947
190	11.65	1137.0	5958.9	4822	0.940
195	12.85	1195.3	6023.2	4828	0.931
200	14.44	1263.4	6087.5	4824	0.942

* N_1, N_2 are the molar fractions of water and of potassium iodide respectively.

Table III

H_2O 77.48 g. KI 22.52 g. $\frac{N_1}{N_2} = 31.26$, C=12.80

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0.90	−39.5	4774.4	4814	0.900
105	1.10	36.9	4838.4	4802	0.924
110	1.31	103.4	4902.4	4799	0.929
115	1.53	165.0	4966.4	4801	0.916
120	1.78	226.7	5030.4	4804	0.908

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
125	2·10	295·3	5094·4	4799	0·917
130	2·44	360·5	5158·4	4798	0·914
135	2·83	424·5	5222·4	4798	0·917
140	3·28	490·7	5286·4	4796	0·919
145	3·78	555·9	5350·4	4795	0·921
150	4·32	619·1	5414·4	4795	0·921
155	4·92	682·1	5478·4	4796	0·918
160	5·58	744·6	5542·4	4796	0·915
165	6·38	811·8	5606·4	4795	0·921
170	7·20	874·7	5670·4	4796	0·923
175	8·02	932·9	5734·4	4802	0·910
180	8·98	994·5	5798·4	4804	0·908
185	10·05	1057·1	5862·4	4805	0·906
190	11·09	1114·2	5926·4	4812	0·895
195	12·30	1174·7	5990·4	4816	0·891
200	13·61	1234·8	6054·4	4820	0·887

Table IV

H_2O 63·37 g.
KI 36·63 g.

$\frac{N_1}{N_2} = 15.95$, $C = 12.68$

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0·83	−69·5	4729·6	4799	0·830
105	1·01	3·8	4793·0	4789	0·841
110	1·18	63·4	4856·4	4793	0·837
115	1·38	125·0	4919·8	4795	0·826
120	1·67	201·6	4983·2	4782	0·852
125	1·92	259·7	5046·6	4787	0·838
130	2·23	324·1	5110·0	4786	0·835
135	2·55	382·0	5173·4	4791	0·825
140	2·96	448·3	5236·8	4789	0·829
145	3·42	514·1	5300·2	4786	0·834
150	3·94	580·1	5363·6	4784	0·840
155	4·49	642·9	5427·0	4784	0·838
160	5·12	707·3	5490·4	4783	0·839
165	5·76	767·0	5553·8	4787	0·832
170	6·46	826·6	5617·2	4791	0·826
175	7·30	890·7	5680·6	4790	0·829

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
180	8·19	952·8	5744·0	4791	0·828
185	9·15	1014·1	5807·4	4793	0·825
190	10·18	1074·6	5870·8	4796	0·822
195	11·20	1130·8	5934·2	4803	0·812
200	12·48	1194·1	5997·6	4804	0·814

Table V

H_2O 50.08 g.
KI 49.92 g.

$\frac{N_1}{N_2} = 9.20$, C=12.53

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0·765	−99·9	4673·7	4774	0·765
105	0·921	31·1	4736·3	4768	0·774
110	1·12	44·4	4799·0	4755	0·794
115	1·30	101·8	4861·6	4760	0·778
120	1·50	159·4	4924·3	4765	0·765
125	1·74	220·5	4986·9	4767	0·760
130	2·05	290·1	5049·6	4760	0·768
135	2·40	357·3	5112·2	4755	0·777
140	2·78	422·3	5174·9	4753	0·779
145	3·15	479·7	5237·5	4758	0·768
150	3·72	544·3	5300·2	4756	0·772
155	4·15	609·2	5362·9	4754	0·774
160	4·71	671·1	5425·5	4754	0·772
165	5·38	737·1	5488·1	4751	0·777
170	6·05	797·6	5550·8	4753	0·774
175	6·80	858·9	5613·4	4755	0·772
180	7·58	917·7	5676·1	4758	0·766
185	8·45	977·4	5738·7	4761	0·762
190	9·36	1035·6	5801·4	4766	0·756
195	10·38	1095·3	5864·0	4769	0·752
200	11·39	1150·8	5926·7	4776	0·743

Table VI

H_2O 45.50 g.
KI 54.50 g.

$\frac{N_1}{N_2} = 7.70$, $C = 12.48$

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0.722	−121.5	4655.0	4777	0.722
105	0.861	−56.6	4717.4	4764	0.724
110	1.07	25.9	4779.8	4754	0.759
115	1.25	86.6	4842.2	4756	0.749
120	1.47	151.4	4904.6	4753	0.750
125	1.70	211.2	4967.0	4756	0.742
130	1.94	267.8	5029.4	4762	0.727
135	2.29	338.1	5091.8	4754	0.741
140	2.65	402.6	5154.2	4752	0.742
145	3.04	464.8	5216.6	4752	0.742
150	3.45	523.9	5279.0	4755	0.736
155	3.93	585.9	5341.4	4756	0.733
160	4.50	651.4	5403.8	4753	0.738
165	5.14	717.2	5466.2	4749	0.743
170	5.81	779.6	5528.6	4749	0.743
175	6.54	841.5	5591.0	4750	0.742
180	7.35	903.8	5653.4	4750	0.743
185	9.19	963.3	5715.8	4753	0.739
190	8.09	1022.1	5778.2	4756	0.734
195	10.10	1077.8	5840.6	4763	0.725
200	10.94	1131.8	5903.0	4771	0.713

Table VII

H_2O 40.00 g.
KI 60.00 g.

$\frac{N_1}{N_2} = 6.14$, $C = 12.45$

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0.712	−126.7	4643.9	4771	0.712
105	0.859	−57.5	4706.1	4784	0.722
110	0.991	−3.5	4768.4	4772	0.703
115	1.12	42.6	4830.6	4788	0.686
120	1.36	120.3	4892.9	4773	0.694
125	1.57	179.8	4955.1	4775	0.686
130	1.83	244.6	5017.4	4773	0.685

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
135	2·16	314·6	5079·6	4765	0·699
140	2·48	375·4	5141·9	4767	0·695
145	2·82	433·4	5204·1	4771	0·688
150	3·26	499·3	5266·4	4768	0·694
155	3·72	562·4	5328·6	4766	0·694
160	4·26	627·7	5390·9	4763	0·698
165	4·85	691·6	5453·1	4762	0·701
170	5·47	752·9	5515·4	4763	0·700
175	6·11	811·0	5577·6	4763	0·694
180	6·87	873·2	5639·9	4763	0·695
185	7·74	937·4	5702·1	4765	0·698
190	8·60	996·4	5764·4	4768	0·694
195	9·57	1057·9	5826·6	4769	0·694
200	10·41	1107·8	5888·9	4781	0·679

Table VIII

H_2O 32·50 g.
KI 67·50 g.

$\frac{N_1}{N_2} = 4.43$, C = 12.43

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
100	0·605	−165·5	4636·4	4802	0·605
105	0·720	−124·2	4698·5	4823	0·605
110	0·902	−39·5	4760·7	4800	0·640
115	1·01	3·9	4822·8	4819	0·605
120	1·22	78·2	4885·0	4807	0·622
125	1·41	136·8	4947·1	4810	0·616
130	1·62	194·9	5009·3	4814	0·607
135	1·90	261·9	5071·4	4810	0·615
140	2·20	326·7	5133·6	4807	0·616
145	2·52	386·4	5195·7	4809	0·615
150	2·95	457·7	5257·9	4800	0·629
155	3·40	523·9	5320·0	4796	0·634
160	3·90	589·4	5382·2	4793	0·639
165	4·44	653·0	5444·3	4791	0·642
170	5·00	713·1	5506·5	4793	0·639
175	5·60	771·9	5568·6	4797	0·636
180	6·25	830·3	5630·8	4801	0·632
185	6·97	889·4	5692·9	4804	0·626
190	7·75	948·2	5755·1	4807	0·626
195	8·55	1004·5	5817·2	4813	0·620
200	9·40	1060·1	5879·4	4819	0·613

Table IX

H_2O 27.05 g. KI 72.95 g. $\frac{N_1}{N_2} = 3.42$, C = 12.19

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
120	*1·12				
125	*1·30				
130	*1·51				
135	*1·76				
140	*2·04				
145	2·32	351·8	4995·4	4644	0·566
150	2·70	420·2	5056·4	4636	0·576
155	3·15	492·3	5117·3	4625	0·588
160	3·60	554·7	5178·3	4624	0·590
165	4·10	618·1	5239·2	4621	0·593
170	4·62	678·1	5300·2	4622	0·591
175	5·17	736·1	5361·1	4625	0·587
180	5·76	793·4	5422·1	4629	0·582
185	6·45	853·9	5483·0	4929	0·582
190	7·20	914·2	5544·0	4630	0·581
195	7·85	964·5	5604·9	4640	0·569
200	8·72	1024·5	5665·9	4641	0·568

The values which are marked * coincide with the vapour pressures of the saturated solution.

Table X

H_2O 24.44 g. KI 75.56 g. $\frac{N_1}{N_2} = 2.98$, C = 11.62

t°C	p (atms)	Tlnp	CT	L/R	p/p_0
140	*2·04				
145	*2·29				
150	*2·61				
155	*2·97				
160	*3·29				
165	*3·76				
170	4·24	640·0	5147·7	4508	0·542
175	4·75	698·2	5205·8	4508	0·539
180	5·31	756·5	5263·9	4507	0·537
185	5·92	814·6	5322·0	4507	0·534
190	6·60	873·9	5380·1	4506	0·533
195	7·30	930·5	5438·2	4508	0·529
200	8·10	989·6	5496·3	4507	0·528

Table XI

H_2O) the saturated solution at each temperature
KI)

t°C	p (atms)	p/p_0	Solubility. gr. in 100g. Solution	N_1/N_2
100	0.606	0.606		4.43
105	0.723	0.606	68.3	4.29
110	0.861	0.611	69.0	4.13
115	0.998	0.596	69.5	4.05
120	1.12	0.571	70.0	3.95
125	1.30	0.568	70.5	3.85
130	1.52	0.570	71.0	3.76
135	1.77	0.573	71.5	3.69
140	2.04	0.571	72.0	3.59
145	2.30	0.561	72.25	3.55
150	2.62	0.559	72.7	3.46
155	2.97	0.554	73.5	3.33
160	3.30	0.541	74.0	3.24
165	3.76	0.543	74.5	3.17
170	4.24	0.542	75.0	3.07
175	4.68	0.531	75.5	2.98
180	5.11	0.517	76.0	2.91
185	5.71	0.515	76.75	2.80
190	6.32	0.510	77.5	2.68
195	6.92	0.502	78.0	2.64
200	7.58	0.494	78.5	2.53

Fig. 3

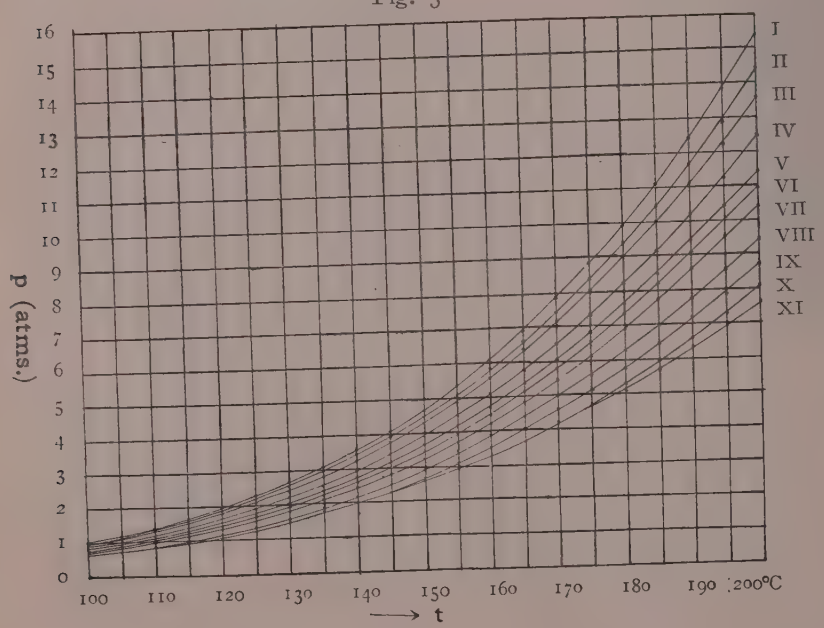
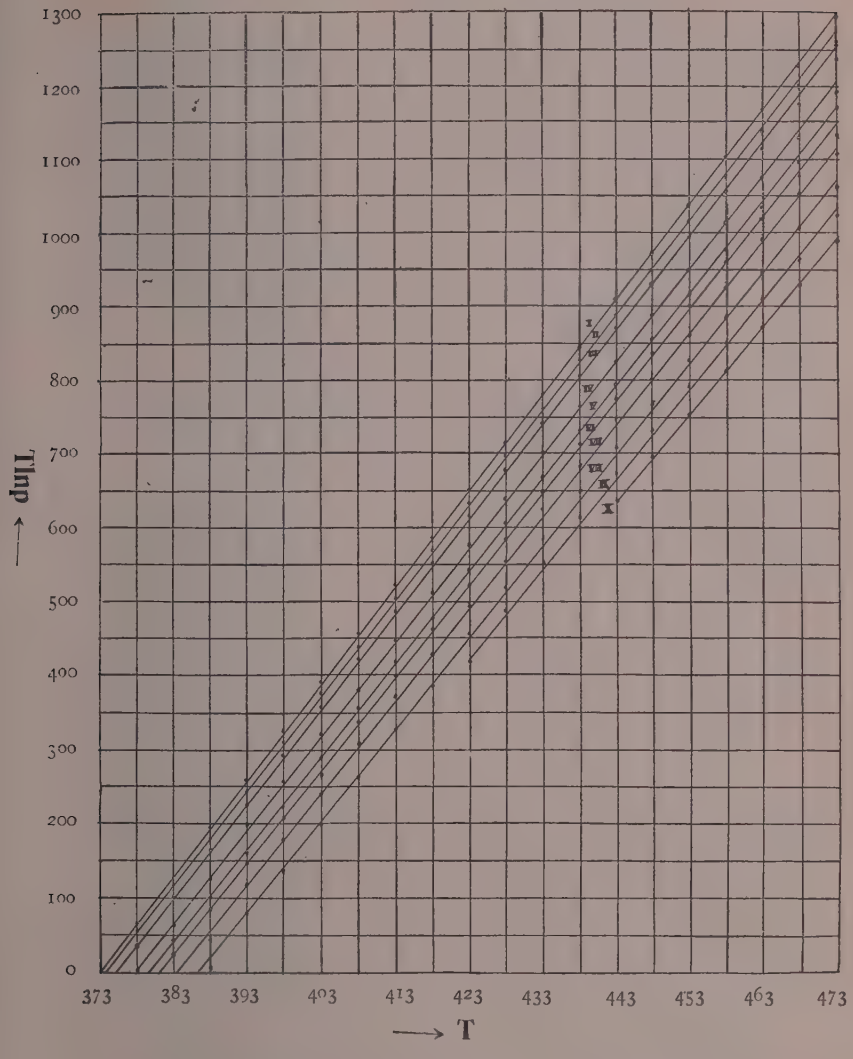


Fig. 4



For comparison, the vapour pressures of pure water quoted from the Landolt Tables are given in Table I.[1]

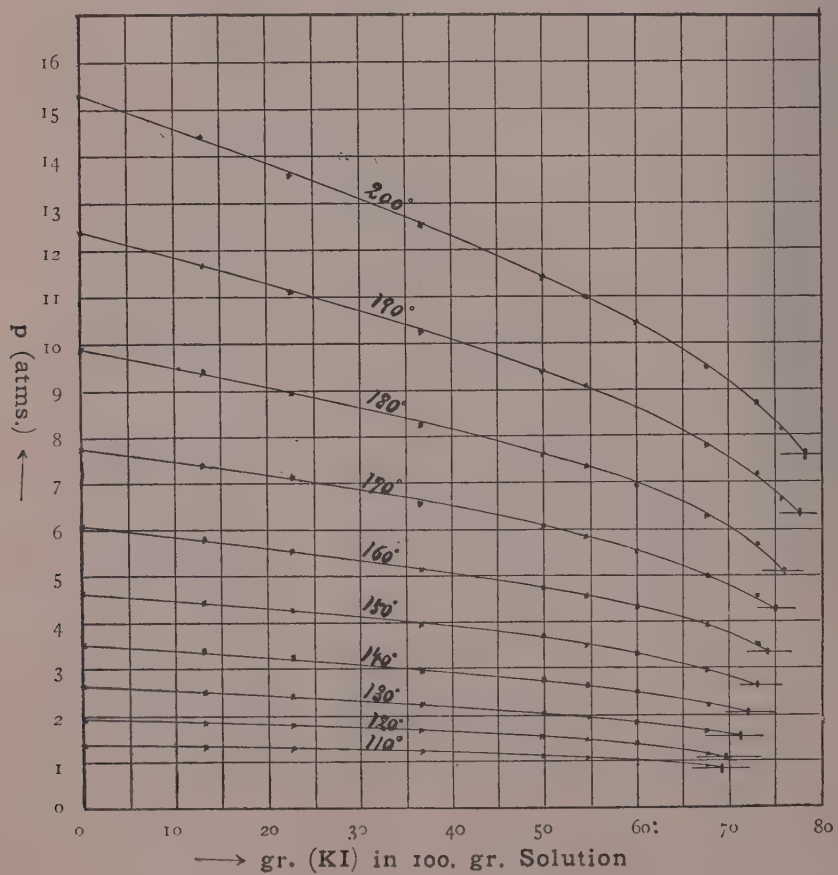
The results obtained are plotted on the pressure-temperature diagram

1. Landolt-Börnstein, Tabellen, 5. Aufl.

in Fig. 3. As may be seen from the diagram, an increase in the concentration causes a fairly remarkable lowering of the vapour pressure. These values stand under p/p_o in the Tables. Curves IX and X coincide with the vapour pressure curve of the saturated solution, which was represented by curves XI, until 140° and 175° respectively, and above these temperatures they move upward from the latter. These are the points which denote the solubilities of potassium iodide at these temperatures.

For the application of the well known Clapeylon-Clausius formula $T \ln p = -\frac{L}{R} + CT$, T—Tlnp curves were plotted from the above experimental results, then we have, as shown in Fig. 4, straight

Fig. 5



lines, running nearly parallel to each other for the solutions of different concentrations and we can easily calculate the value L and C. But, exactly speaking, a slight difference of inclination exists between these straight lines and in fact the constant C varies with the concentrations of the solutions, as 13.05, 12.87, 12.80, etc. The term C has a close relation with the internal pressure of the solution, and its change with the concentration would be of interest from the theoretical standpoint of concentrated solutions, and the writer leaves it for later study.

The heats of vaporization L, calculated from the Clapeylon-Clausius formula, are also shown in the Tables.

Calculation of the Solubility

The determination of the solubilities of the substance in water at higher temperatures is very difficult, and so it is very remarkable that from the results now obtained the calculation of solubility appears to be possible. Theoretically the points where the isothermals reach the height of the vapour pressures of the satulated solutions at the respective temperatures on the concentration-vapour pressure diagram show the solubilities at those temperatures. These relations can easily be gathered by Fig. 5, and Table XI gives the solubilities thus obtained. They agree fairly well with the above information as to the curves IX and X. The solubility curve now obtained also continues smoothly with the solubility curve below 100°C measured by Mulden,[1] and as a whole, the increase of solubility is linear with respect to temperature.

Activity.

From the results obtained above the activities of the solvent can easily be calculated. The expression of the activity for the solvent is

$$a_1 = \frac{p}{p_o}\ ; \quad \text{already given in Tables I——XI.}$$

As to the activity of the solute, the expression is

$$ln\ a_2 = -\int_o^{N_2} \frac{N_1}{N_2} d\ ln\left(\frac{p}{p_0}\Big/ N_1\right),$$

where N_1 and N_2 are molar fractions of solvent and solute, p the vapour pressure of the solution and p_o that of the solvent. The integration of this equation cannot be wholly carried out because of the lack of

1 Landolt-Börnstein, Tabellen, 5 Aufl., 1, 661.

the measurements at dilute concentrations.

Summary.

1) The vapour pressures of the concentrated aqueous solutions of potassium iodide were measured at various concentrations. The heats of vaporization of these solutions were calculated and it was noted that the values of C in the Clapeylon-Clausius equation vary with the concentration.

2) The solubilities of potassium iodide at high temperatures were calculated from the data of the vapour pressures.

3) The activities of the solvent were calculated.

The writer wishes to express his hearty thanks to professor S. Horiba for his kind and helpful directions.

May, 1927

Laboratory of Physical Chemistry.

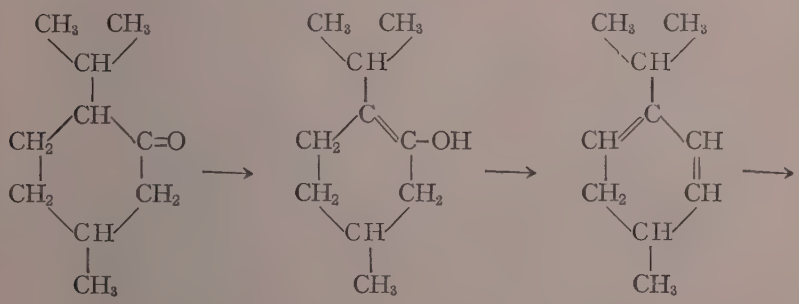
Studies on Catalytic Action, XXII. Catalytic Action of Reduced Copper on Unsaturated Hydrocarbons.

By

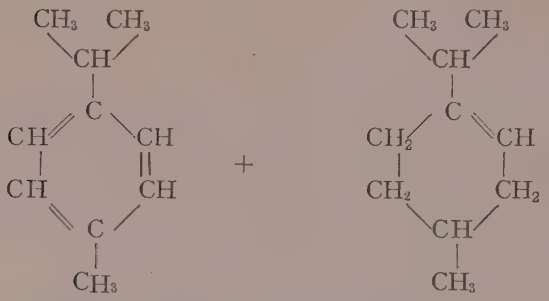
Shigeru Komatsu and Masao Kurata.

(Received Feb. 8, 1928)

In the course of the catalytic action of reduced copper on menthone at 300°, the writers noticed the occurrence of thymol, cymene and menthene in the reaction product, and the formation of these hydrocarbons from menthone was explained as follows[1]:



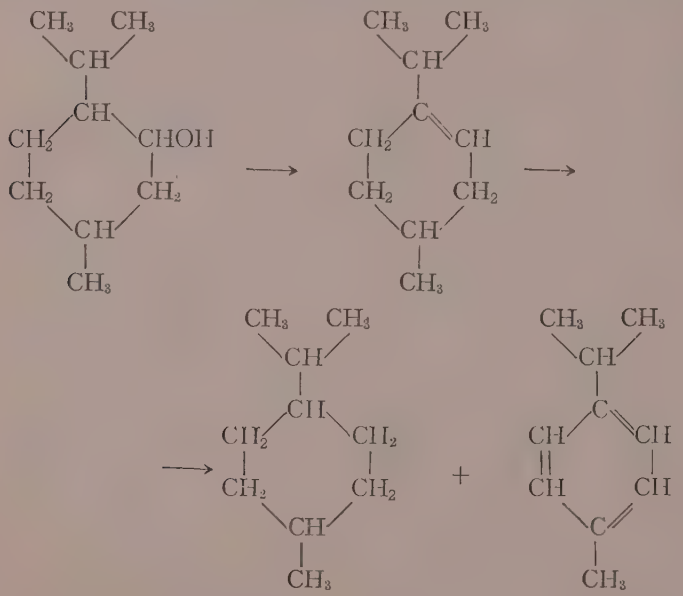
1 These Memoirs: A, **9**, 23 (1925).



The menthadien formed as an intermediate reaction product, by the dehydration of menthenol resulting from the keto-enolic transformation of menthone, was converted by catalytic oxidation and reduction taking place simultaneously, into menthene and cymene.

Admitting that the assumption for the formation of these hydrocarbons was correct, the index of refraction of the fraction of hydrocarbons being $n_D^{25} = 1{\cdot}4599$ indicated that the fraction composed of cymene and menthene in a mole ratio of 43:57.

The formation of cymene and menthane from menthol by the contact action of reduced copper and reduced nickel heated at 200°,[2] will also be expressed analogously by the following interpretation:



2 Ibid., A, 8, 35, 65 (1925).

The other cases which would provide examples of the non-reversible catalysis of unsaturated hydrocabons have been previously mentioned by one of the present writers (S. K.) and his co-workers[1] in the occurrence of naphthalene and dihydro– and tetrahydronaphthalenes in the course of the catalytic reduction of the α– and β–naphthyl ethers in the presence of reduced nickel heated at 200°, and of benzene and its hydrogenated compounds in the reaction products from cyclohexanol or cyclohexyl amine by the contact action of reduced copper.

The non-reversible catalysis of the unsaturated hydrocarbons was already noticed by H. Wieland on the study of dihydronaphthalene which by shaking with platium black dissolved in benzene, yields naphthalene and tetrahydronaphthalene.[2]

The conversion of the incompletely hydrogenated aromatic hydrocarbons, such as cyclohexene, menthene and limonene, into aromatic hydrocarbons and a saturated cyclic compound was noticed by N. Zelinsky and his co-workers, in which finely divided platinum, palladium, iridium and nickel were noticed to serve as possible catalysts in this reaction.[3]

In order to verify whether cymene and menthane or naphthalene and tetrahydronaphthalene were formed by non-reversible catalysis or some other reaction from menthene or dihydronaphthalene which were regarded as being formed as an intermediate reaction product from menthol or tetrahydronaphthol by dehydration respectively, the present investigation was undertaken with menthene, limonene and β–phellandrene as a starting material.

The reduced copper used in the reaction was prepared by reduction with hydrogen at 200° from copper oxide formed by the action of a dilute caustic soda solution on copper sulphate.

Menthene.

Menthene was prepared from l–menthol by passing on thoria heated at 400°, and purified as usual, and the physical constants of the hydrocarbon were mentioned in the table.

54 gm. of pure menthene were passed on reduced copper prepared from 10 gm. oxide which was heated at 290–300°, at a rate of 4.5 gm. per hour; hydrogen gas was noticed to evolve only at the beginning of the reaction and amounted to 450 c.c. (at 0°, 760 mm.) The

1 These Memoirs: A, **7**, 135 (1924); A, **8**, 135 (1925); A, **9**, 15 (1925)
2 Ber. D. Chem. Ges., **45**, 486 (1912).
3 Ibid., **56**, 1723 (1923); **57**, 1066, 1070, 2055 (1924); **53**, 864 (1925); **60**, 1096 (1927); and also refer: Böeseken: Rec. trav. chim., **37**, 255 (1918).

reaction product which shows the physical constants shown in the table, was confirmed to consist of cymene and menthane with unchanged menthene.

Menthene in the reaction product was confirmed by converting into nitrosochloride showing M.p. 127° $[\alpha]_D = +17.28°$

Cymene. The occurrence of this compound in the reaction product was confirmed by transforming into p-oxy-isopropyl benzoic acid M. p. 156°–157°. However, the yield of the acid from the reaction product by oxidation was very samll owing to the presence of menthene in it, which prevents the oxidation of cymene, as we learnt from the behaviour of the oxidizine agent in the mixture of cymene and menthene.

In the isolation of menthane from the reaction product, 30 grm. of the sample were treated with a 10 % fuming sulphuric acid solution at 5° to free menthene and cymene from menthane by converting them into soluble forms in sulphuric acid, and the residual oil amounting to 5.1 grm., was treated again with fuming sulphuric acid. 3 grm. of oily substance which had escaped from the reaction from the sulphuric acid, were distilled on metallic sodium, the fraction (B. p. 165°–168°) amounted to 2.5 grm., which shows $n_D^{25} = 1.4332$; $d_4^{25} = 0.7889$; M.R.=46.14; and was optically inactive. It decolorizes neither bromine nor potassium permanganate and the properties agree with those of menthane.

The non-reversible catalysis of menthene in the presence of reduced copper heated at 300°, by the study of the chemical and the physical properties of the reaction products, was observed actually to happen, resulting in the formation of cymene and menthane.

$$3\ C_{10}H_{18} = C_{10}H_{14} + 2\ C_{10}H_{20}$$

d-Limonene.

Pure d-limonene from Theodor Schuchardt, of the properties shown in the table, by passing on reduced copper heated at 280°-300°. was converted completely into cymene.

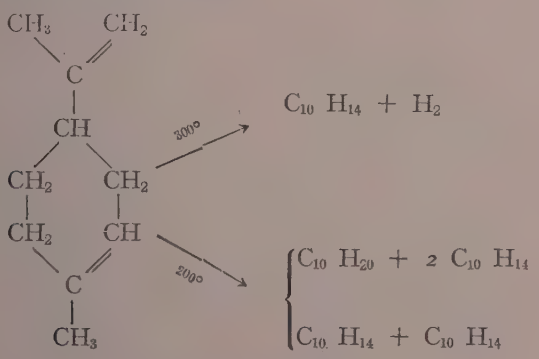
When, however, 4·5 grm. of limonene were passed on the catalyst heated at 200,° during an interval of one hour, no hydrogen was evolved, and 4·2 grm. of the reaction product of the physical properties shown in the table were obtained, which was subjected to fractional distillation :

Fraction	Yield	n_D^{25}
1. B.p., 169°–172°	0·8 grm.	1·4670
2. " 172°–175°	2·6 "	1·4679
3. " 175°–177°	0·5 "	1·4692
	3·9 "	

The first fraction was treated with conc. sulphuric acid and the remaining oil showed $n_D^{25} = 1{\cdot}4605$ which indicates the occurrence of cymene and menthane in it. The latter substance was isolated from the mixture by treating it with fuming sulphuric acid and the resulting oil shows B.p. 165·–168°, $n_D^{25} = 1{\cdot}4331$. The occurrence of dipentene in the second fraction B.p. 172°–175°, was proved by converting it into dipentene tetrabromide M.p. 124°.

The second fraction was also found to consist of limonene and carvomenthene by isolating the nitrosochlorides which possessed the same melting-points as limonene nitrosochloride M. p. 100°–103°, and also carvomenthene nitrosochloride M.p. 94°–95°. The formation of carvomenthene from limonene was reported by G. Vavon[1] by subjecting it to partial reduction in the presence of platinum black.

The behaviour of d-limonene towards the reduced copper will be represented in the following scheme:



d–β– Phellandrene.

d–β–Phellandrene from Theodor Schuchardt, purified by distillation

1 C. R., **152**, 1677 (1911).

under reduced pressure, indicating the physical constants shown in the table, was passed in a glass tube heated at 300°, and 2·6 grm. of the product were obtained from 3 gm., of the sample, and the product shows the constants of pure phellandren:

$[\alpha]_D = +6{\cdot}72$ (in $\frac{1}{2}$ dm. tube); $d_4^{25} = 0{\cdot}8401$; B.p. 170°–175°.

When 5·3 grm. of phellandrene were passed on the reduced copper heated at 300°, during a period of 2 hours, 5·2 grm. of the reaction product having the physical properties shown in the table, were obtained. In the course of the reaction, hydrogen gas was evolved continuously, and the total volume was estimated to be 411 c.c. under normal conditions (0°, 760 mm.) which are equivalent, by assuming that the conversion of phellandren by catalytic oxidation into cymene has happened, to the quantity of hydrogen generated from 2·47 grm. of phellandrene:

$$C_{10}H_{16} \longrightarrow C_{10}H_{14} + H_2$$

The reaction product indicates, faintly as we had anticipated, its unsaturated character toward potassium permanganate, and also absorbs hydrogen in presence of palladium black. The occurrence of cymene and menthane in the reaction product was confirmed as usual by isolating these compounds, and the percentage of cymene in the product was calculated to be 82·5 % by assuming that the reactions shown in the following schemes take place simultaneously.

$$6\ C_{10}H_{16} \longrightarrow \begin{cases} 3C_{10}H_{14} + 3H_2 \\ C_{10}H_{20} + 2C_{10}H_{14} \end{cases}$$

This value agree quite well with the calculated value, 82 % of cymene, by means of the index of refraction of the reaction products.

So far as the writers have investigated, monocyclic terpenes such as menthene, d-limonene and β-phellandrene, were converted, as we had expected, by non-reversible catalysis of reduced copper into cymene and menthane, and the reduced copper shows the behavior toward these unsaturated hydrocarbons similar to nickel and palladium, though the velocity of the reaction depends largely upon the constitution of the hydrocarbons.

* * *

* *

Table

	B. p	α_D (l = 1dm.)	d_4^{25}	n_D^{25}	n_α^{25}	$n_\beta - n_\alpha$	$n_\gamma - n_\alpha$
Menthene: Sample	165–167°	+30.42°	0.8066	1.44956	1.44492	0.01123	0.01667
Menthene: Reaction product at 300°	—	+21.95°	0.8060	1.45137	1.44852	0.00956	0.01533
Limonene: Sample	175–176.5	+103.72°	0.8389	1.47082	1.46786	0.01094	——
Limonene: Reaction product at 200°	172–175°	− 0.12°	0.8498	1.48750	1.48379	0.01383	——
Limonene: Reaction product at 300°	169–178°	+ 62.00°	0.8333	1.46817	1.46525	0.01088	——
β-Phellandren: Sample	65–67° *	+ 16.42°	0.8448	1.47674	1.47335	0.01200	0.01961
β-Phellandren: Reaction product at 300°	166–174°	+ 0.38°	0.8377	1.47650	1.47325	0.01337	0.02073

* at 12mm.

April 1925, Laboratory of Organic-and Bio-Chemistry.

On the Transformation of Aliphatic Terpenes into Monocyclic Terpenes-A Synthesis of Menthol.

By

Riki Horiuchi.

(Received March 24, 1928)

The transformation of aliphatic or olefinic terpenes of the formulae $C_{10}H_{18}O$ & $C_{10}H_{18}O$ into their isomeric monocyclic terpenes is very interesting from the stand points of synthetic chemistry on the one hand, and, on the other of biochemistry.

Citral, the principal constituent of oil of lemon and of lemon-grass was employed to prepare by cyclisation of its derivatives, the ionones which are used as a synthetic substitute for the odorous principle of the violet.[1] Monocyclic terpene, isopulegol or menthone had been obtained from the olefinic terpenes of citronellal and rhodinal respectively by the action of acetic anhydride,[2] and the very close relationship between the cyclic terpenes and the open chain ones show that these compounds exhibit among themselves a certain similarity in structure, and this relationship has been used for the confirmation of the structure of citronellal.[3] The cyclisation of the olefinic terpenes, especially of citronellal, awakes the interest of certain chemists among whom F. Tiemann & R. Schmidt[1] were the first who attempted the transformation of the aldehyde

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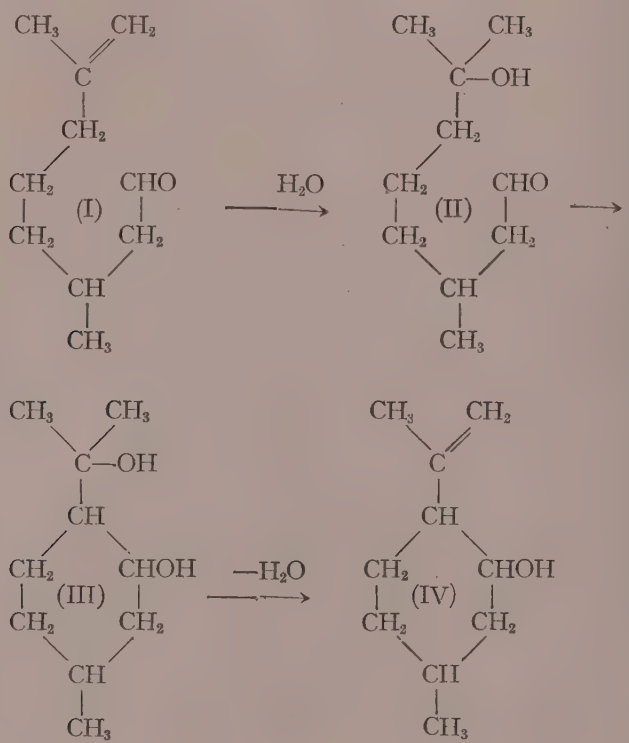
1 F. Tiemann: Ber. D. Chem. Ges., **26**, 2675 (1893).

2 F. Tiemann & Schmidt: Ibid., **30**, 38 (1897).

3 F. Tiemann & R. Schmidt: Loc. cit., P. Barbier & G. Leser: C. R., **124** 1308 (1897); C. Harries & G. Roeder: Ber. D. Chem. Ges., **32** 3357 (1899) Loc. Cit.,

by heating with acetic anhydride and anhydrous sodium acetate in a sealed tube at 180°–200° for 10–12 hours, and acetate of isopulegol was isolated.

P. Barbier & G. Leser,[1] however, have succeded in transforming citronellal by the action of a 5% sulphuric acid into isopulegol, menthoglycol or menthanediol (3 : 8) and a compound of the formula $C_{20}H_{34}O$ of ethereal character, and in this reaction they stated that citronellal (I) is probably first transformed by the addition of water into hydroxycitronellal (II) and then ring formation occurs with the production of menthoglycol (III) which then turns by the removal of water to isopulegol (IV) as represented in the following:

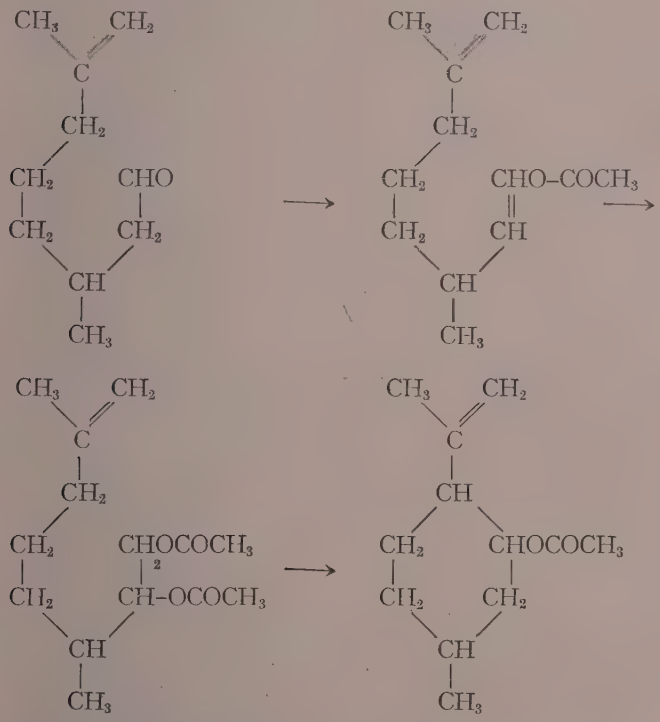


The latter phase of the reactions, the formation of isopulegol was demonstrated by them with an experiment in which monoacetate of

1 Loc. Cit.

menthoglycol was converted by treating with sodium acetate into acetate of isopulegol.

With regard to the mechanism of the cyclisation of the olefinic terpene, F. W. Semmler[1] has proposed another view that aldehydes of the types RCH=CHO or RCH_2CHO are converted to the enolic forms by acetic anhydride and that in the case of citronellal this change precedes ring formation; enol monoacetate and enol di-acetate of citronellal have resulted by the action of acetic acid and sodium acetate on citronellal and the process for the transformation of citronellal into the cyclic terpenes has been represented by the scheme shown below since the enol monoacetate can be converted into isopulegol acetate by heating with acetic anhydride for 20 hours.

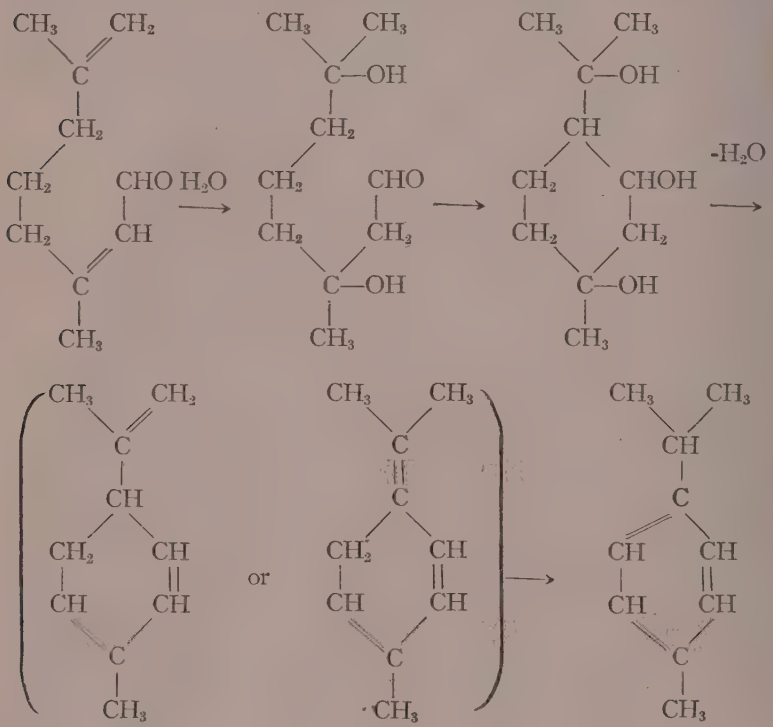


The fact that citral yields, by the action of acetic acid & sodium acetate, enol monoacetate and enol di-acetate of citral and that cymene

1 Ber. D. Chem. Ges. **42**, 2015 (1909).

was formed from citral by the action of potassium hydrogen sulphate and also from enol acetate citral by treating with acetic acid,[1] were regarded by Semmler to be favourable examples of his view of the cyclisation of open chain-terpenes.

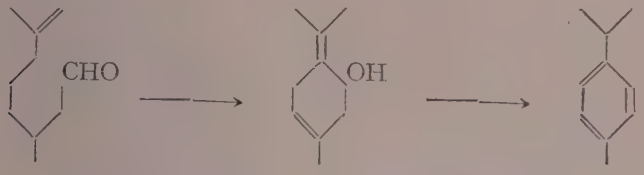
According to F. Tiemann[2], the cause of the formation of cymene from citral by the action of a 10% sulphuric acid should be attributed, as Barbier and Leser had explained the formation of isopulegol from



citronellal, to the intervention of water which is alternately added and removed. The above views illustrated by Tiemann, Semmler and Barbier show how difficult it is to explain the formation of dehydro-isopulegol or methyl isopropene cyclohexanol from citral, which, according to A. Verley,[3] was produced from citral by the action of a 50% sulphuric acid

1 F. W. Semmler & Schossberger: Ber. D. Chem. Ges., **44**, 991 (1911).
2 Ibid., **32**, 107 (1899)
3 Bull Soc. Chim., **21**, 408 (1899).

in an ethyl acetate solution, and by the action of dehydrating agents it gives rise to cymene :



The writer holds an opinion somewhat different from the views above mentioned, for the explanation of the cyclisation of the olefinic terpenes, ascribing the cause of the reaction to the direct condensation between the $=CH-CH_2-$ and the $CHO-CH_2-$ groups which occur in the molecule, and he considers that the keto-enolic change of the $CHO-CH_2$ – group was not the primary cause of the reaction. To confirm the above hypothesis, citral and citronellal were subjected to the action of sulphuric acid of various concentrations and of potassium hydrogen sulphate and acetic acid, and the reaction products surveyed with meticulous care.

d–Citronellal isolated in pure state from the Java citronella oil,[1] B.p. 97°—98° at 20 mm.; $d_{15}^{15} = 0.8563$; $n_D^{20} = 1.449$; $a = +10°.9'$, when treated with 5% sulphuric acid at ordinary temperature, yields isopulegol, menthoglycol and a compound of the formula $C_{20}H_{36}O_2$ of ethereal nature, and the experimental results agree with those of Barbier & Leser[2] except for the formation of the last compound of which having the physical constants, B.p. (196°–198°) 18mm; $d_4^{20} = 0.9295$: $n_D^{20} = 1,4805$, and appears to be different from the bispulegone obtained by Harries & Roeder by reducing pulegone with an aluminium amalgam.[3]

	Yield		
conc. SO_4H_2	Isopulegol	Menthoglycol	Ether
5%	7%	75%	3%
20%	9%	39%	21%

1 H. Finnemore: The essential oils (1926) 118.

2 Loc. cit.,

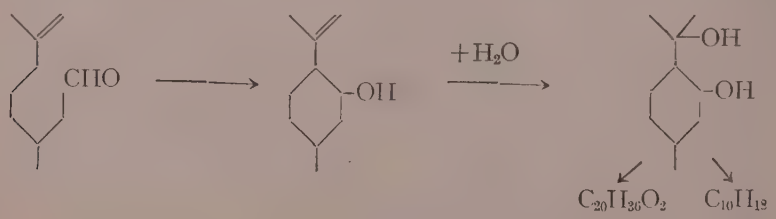
3 Ber. D. Chem Ges., **32**, 3357 (1899), and refer V. Paolini: J. Chem. Soc., **118**, 171 (1920).

The yield of the glycol as will be seen in the table, will be increased in inverse proportion to that of the ethereal compound, while isopulegol was formed with a greater yield in the higher concentration of the acid, used as a condensing agent. It seems, therefore, that the isopulegol formed directly from citronellal by the action of the condensing agent was converted into menthoglycol by the addition of water, on the one hand, and on the other, by the removal of water it turns to the other-compound.

As a matter of fact, isopulegol when treated with a 20% sulphuric acid, yields menthoglycol, while the latter substance under the same treatment remains unchanged. Moreover, citronellal, subjected to the action of a 50% sulphuric acid, resulted in forming a new terpene $C_{10}H_{16}$; B.p. (60°—90,°) 14mm; $d_4^{20} = 0.8535$; $n_D^{20} = 1.4875$ and the ether $C_{20}H_{36}O_2$ instead of forming either the glycol or isopulegol, and both the terpene and ether are also produced, in different proportions, from isopulegol and menthoglycol respectively by treating with strong sulphuric acid, referring to the fact that the terpene is predominant in the reaction product from the glycol while the ether occurs abundantly in that from the isopulegol, and also to the investigation by Senderens[1] of the

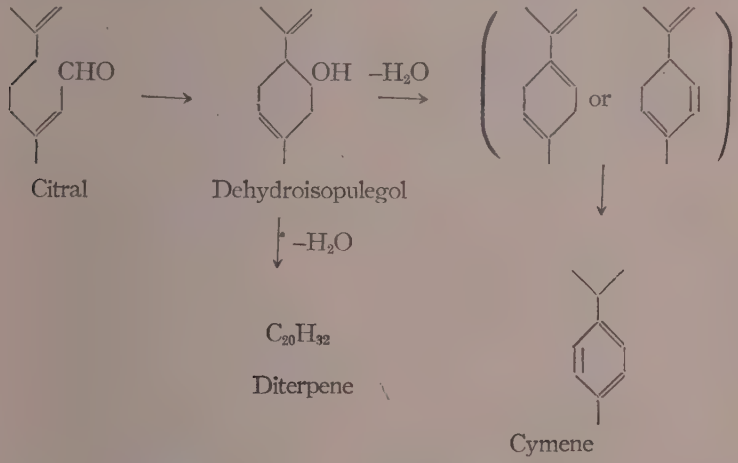
Material	Yield	
	Terpene	Ether
Isopulegol	20%	36%
Menthoglycol	44%	18%
Citronellal	14%	32%

action of sulphuric acid on the polymethylene alcohols and by Wallach[2] on menthenols, the writer has proposed the view on the transformation of citronellal into cyclic terpenes, which is indicated in the following scheme:



1 C.R., **177**, 1183 (1923).
2 Liebig Ann., **360**, 82 (1908).

By the action of the 20% & 50% solutions of sulphuic acid on citral, a new terpene $C_{10}H_{14}$, b.p. 183°—186°, $d_4^{20} = 0.8880$; $n_D^{20} = 1.5092$ and p-cymene were respectively isolated from the reaction products, and a diterpene $C_{20}H_{32}$, b.p. (194°–199°) 17mm., $d_4^{20} = 0.9494$; $n_D^{20} = 1.5303$, and cymene were formed to occur in the product from citral by the action of potassium acid sulphate, and these compounds should be derived from the dehydro isopulegol which was supposed to formed from citral as an intermediate product, and previously isolated by Verley.[1]



When citronellal is treated with potassium hydrogen sulphate, a violent reaction takes place suddenly when the temperature has risen to 140,° and isopulegol and the ether $C_{20}H_{36}O$, B.p. (185°) 12mm., $d_4^{20} =$ 0·9120; $n_D^{20} = 1.4835$ are obtained and the latter substance is identical in property with di-isopulegol ether prepared by Verley, The ether was actually prepared from isopulegol, and also from menthoglycol, by the action of potassium hydrogen sulphate, and in the latter case a terpene is found to occur with the ether in the reaction product.

When, however, acetic anhydride and sodium acetate were used as the condensation agent, citronellal tended to yield as reported by Semmler, isopulegol-acetate, enol monoacetate and enol di-acetate of citronellal

1 Loc. Cit.

in a molecular proportion of 20 : 34 : 30. On the contrary, isopulegol acetate and enol di-acetate of citronellal, and isopulegol and isopulegol acetate were found to be formed when acetic anhydride and acetic acid were used respectively as the condensing catalyst.

As will be seem in the above statements, the cyclisation of citronellal is favourable in case acetic acid or acetic anhydride was used, and citral, in a like manner, by the action of acetic anhydride and acetic acid was converted partly into enol acetate of citral and cymene respectively.

According to the experiments carried out by the writer, the diacetate of enol-citronellal yields by the action of acetic acid neither isopulegol nor its derivative, while according to Semmler, the mono acetate of the enol compound by means of acetic acid converted into isopulegol acetate, and therefore the cyclisation of the olefinic terpenes should be ascribed to the inner condensation between the atomic groups $CHO–CH_2–$ and $—CH=CH—$ in the molecule, but not to the enolisation of the group $—CH_2—CHO$ as stated by Semmler.

The fact that the conversion of the olefinic terpenes into isomeric monocyclic terpenes, no matter what may be the correct theory by which the explanation of this transformation was made, still awakens the writer's interest in connection with the origin of the monocyclic terpenes in plants, in getting a clear understanding of the manner of occurrence of these compounds.

On turning our attention of the natural essential oils, we noticed that pulegones and isopulegones occur in nature associated with menthone, oil of pennyroyal, (*Mentha Pulegium*[1]), contains limonene, pulegone with menthol, and in American hedema oil contains about 24 to 30 per cent of pulegone with 50 per cent of menthones.[2]

On the biochemical connection of these cyclic terpenes and olefinic terpenes, in peppermint oil, R. E. Kremers[3] has made the following observation: "pulegone (& possibly piperitone) is found by Schimmel & Co. in Japanese peppermint oil and was regard as a mother of menthol, and it is suggested that menthenone is first formed from citronellal and that menthol and menthone are formed from its reduction."

Therefore, the reduction of pulegones or pulegols to menthols seems to take an important place in the biochemical connection between the

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1 Tetry: Bull. Soc. Chim., **27**, 186 (1902).

2 Finnemore: The essential oils, P. 798 and refer: V. Grignard & I. Savard: C. R., **182**, 422 (1926); V. D. Roberts: J. Chem. Soc., **107**, 1465 (1915).

3 J. Biol Chem., **50**, 31 (1922).

olefinic and the monocyclic terpenes in nature. However, the reduction of pulegone and pulegol and their isomeric compounds in vitro was stated by Tiemann and Schmidt[1] in the following words:

"Pulegon und Pulegol lassen sich durch Natrium und Alkohol unschwer zu Menthol redugiereu; die directe Umwandlung von Isopulegon und Isopulegol in Menthol auf gleichem Wege ist dagegen trotz haufig wiederholter Versuche bis lang nicht gelungen——."

No one could reduced isopulegone or isopulegol into menthol, while the former substance on treatment with baryta undergoes isomeric change to pulegone.[1]

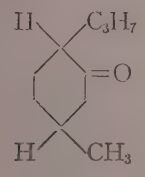
The writer, however, has succeeded in reducing isopulegol which was isolated from isopulegol acetate by hydrolysis and boils at (91.°5) 13 mm.; $d_4^{20}=0.9162$; $n_D^{20}=1.4710$; $\alpha=-30'$, yield by reduction with hydrogen in the presence of platinum block, menthols, of the following constants:

B.p. (103.°5—105.°5) 18. mm; m,p. 1°—10,°

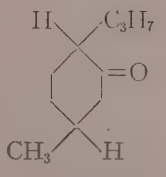
$d_4^{25}=0.8944$; $n_D^{25}=1.458$; $[\alpha]_D=-16.°\ 77'$.

It was fractionated several times under reduced and ordinary pressure, and the fraction B.p. 210°-211°, M.p. 33°-34°, $[\alpha]_D=-44.°92$ was isolated, which was assumed to be pure l-menthol.

In theory, there should exist 8 isomers in menthol and 4 isomers in menthone, and the relationship between menthones & menthols with respect to the special configuration, according to the view proposed by S. Komatsu & M. Kurata[2] is as follows:



d, l-Isomenthone
(cis)



d, l-Menthone
(trans)

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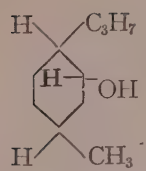
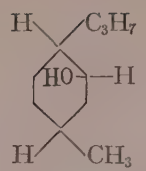
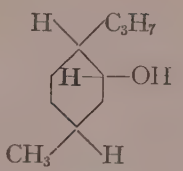
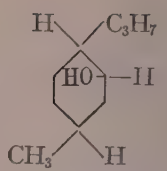
1 Ber. D. Chem. Ges., **25**, 32 (1897).

2 These Memoirs A. **8**, 251 (1925) & refer I. Read: Chem. Ind., **46**, 873 (1927).


d, l–Neoisomenthol
(cis-cis)


d, l–Isomenthol
(trans–trans)


d, l–Neomenthol
(cis–trans)


d, l–Menthol
(trans–cis)

For identification of the writer's sample, it was oxidized by the usual method to menthone which was confirmed by referring to its physical and chemical properties and also by converting it into the oxime, to be laevomenthone. The mother substance which by oxidation yields l–menthone, according to the theory proposed by S. Komatsu and M. Kurata, should be either laevomenthol or neomenthol.

Referring to the literature concerning the properties of menthols we have learned that the present writer's menthol would be composed mostly of laevo–menthol which occurs in nature as a principal constituent of Japanese peppermint oil, and neomenthol is usualy obtained by synthesis.

Brunel[1] has claimed that α & β thymomenthols were synthesized from thymol by reducing by Sabatier's method, and the α—compound was identical with neomenthol, and β one was r-menthol.[2] By the hydrogenation of pulegone,[2] in a manner similar to that of thymol, Haller and Martine[3] obtained two menthols which evidently are identical with leavo-menthol and dextroneomenthol and the same results were obtained by V. Paoline[4] by reducing pulegone by means of sodium and alcohol. According to Smith & Read,[5] however, d, l or r-piperitone by catalytic reduction in the presence of reduced nickel or colloidal palladium yielded isomenthones, and by means of sodium and alcohol yielded a product which appeared to consist essentially of isomenthol.

So far as concerns the reduction of thymol, piperitone or menthone

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1 C.R., **140**, 252 (1905).
2 J. prac. Chem., **55**, 14 (1897); and refer Kondaknow: Ibid., **72**, 185 (1905). Urban & Kreemers: Bull. Soc. chim., **12**, 1439 (1894); Pichard and Littlebury: J. Chem. Soc., **101**, 109 (1912).
3 C.R., **140**, 1298 (1905).
4 J. Chem. Soc., **118**, 171 (1920).
5 Ibid., **123**, 2916 (1923) and refer J. Read: Chem. & Ind., **46**, 873 (1927).

it would seem that the reaction will proceed to form neomenthol.[1]

Piperitone, menthone and pulegone, when submitted to reduction, should theoretically yield an equimolecular mixture of menthol and neomenthol or of isomenthol and neoisomenthol, actually in practice produces only one of the isomers, and this fact would be explained plainly by the theory of asymmetric synthesis; the starting materials for the syntheis of menthol are of optically active substances to which by the operation a new radical is added in such a way as to form a new asymmetric carbon atom, and consequently the original asymmetric nucleus has governed the progress of the reaction to such an extent as to preclude the formation of one isomer.

However, in the writer's synthesis of menthol, it is quite different, in the stereochemical relation of the resulting substances from the above cases; by hydrogenation of the isopulegol molecule, no asymmetric carbon atom was formed; but the relative magnitude of the masses of the carbon radicals attached to the asymmetric carbon atoms already present in the molecule will be changed by this treatment, and there should be a corresponding change in rotatory power of the substance as required by the theory of Guye and Crum Brown.

In the reaction of the formation of active isopulegol by the condensation of citronellal a similar operation is probably carried out in the natural synthesis of l-menthol in plants, which will be fully explained by taking the principle of asymmetric synthesis into consideration.

In tracing back the reactions for the synthesis of laevomenthol, step by step, menthol to isopulegol, isopulegol to citronellal, and citronellal to valeraldehyde, the operations which take place in the plant tissues seem evidently to be imitated in the laboratory.

Experiment.

1. CITRONELLAL.

1. Action of 5% Sulphuric Acid on Citronellal.

Citronellal isolation from the Java citronella oil and purified by means of sodium hydrogensulphite and by distillation shows the following constants:

B.p. 97°–98° at 20 mm., $d\,{}^{15}_{15}=0.8563$, $n_D^{20}=1.4490$; $[\alpha]_D=+10°\ 9'$

It was treated with 10 times by weight of 5% sulphuric acid at 25°–30° for 12 hours, following the direction put forward by P. Barbier

1 G. Vavon & A. Conderc. C. R., **179**, 405 (1924); P. Beds: Bull. Soc. Chim., **29**, 674 (1926).

& G. Leser,[1] and the reaction product separated from the acidic solution, washed with water, dried with anhydrous sodium sulphate and then subjected to fractional distillation under 18 mm.

	Fraction	Yield Wt. %	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	80°—100°	7	0.9123	1,4692	—
2	100°—145°	trace	——	1.4710	—
3	145°—160°	7	0.9687	1,4730	—
4	160°—175°	76	0.9751	1.4730	—
5	175°—185°	3	0.9699	1.4726	—
6	185°—191°	2	0.9540	1.4740	—
7	191°—195°	5	0.9408	1.4769	−4° 48′

Isopulegol.

The first fraction was found to be composed of isopulegol by repeated distillation, which show the following physical constants.

B.p. 202°—207°; $d_4^{20}=0.9087$; $n_D^{20}=1.4672$;

$[\alpha]_D = +5° 4'$; M.R.=47.1; 47.2 for $C_{10}H_{18}O$.

For confirmation, it was oxidized with chromic acid to isopulegone which yields an oxime of m.p. 121.°

Menthoglycol.

The fourth fraction which composed the main part of the reaction product, was analysed:

0.1027 grm. gave 9.2619 grm. CO_2 & 0.1079 grm. H_2O., found C=69.6; H=11.7; theory requirs C=69.8; H=11.6 for $C_{10}H_{19}O_2$. M.R.=49.5; theory M.R.=49.2 for $C_{10}H_{18}O_2$.

It was fractionated under 15 mm. pressure and was divided into three portions which were ascertained to be composed mostly of menthoglycol by referring to their properties as follows:

	Fraction	%	d_4^{20}	n_D^{20}	$[\alpha]_D$	M.P.
1	147.5°	34	0.9833	1.4710	+37′	62°
2	148°—151°	26	0.9833	1.4710	+5° 23′	liquid
3	151°—152°	40	0.9797	1.4700	0	"

An Ethereal Compound.

The 7th fraction which was assumed to be composed of an unsaturated compound of ethereal nature, and its acetic acid solution

1 Loc. cit.,

was reduced with hydrogen in the presence of platinum black and the product shows the constants:

$$d_4^{20}=0.9180; \qquad n_D^{20}=1.4640.$$

2. Action of 20% Sulphuric Acid on Citronellal.

The citronellal was treated with 20% sulphuric acid in the manner described above and the reaction product was fractionated under 16 mm. pressure into the following 6 portions:

	Fraction	Yield	d_4^{20}	n_D^{20}
1	75—110°	9%	0.9181	1.4730
2	110—140°	3%	0.9283	1.4700
3	140—160°	40%	0.9654	1.4729
4	160—185°	3%	0.9581	1.4731
5	185—195°	42%	0.9287	1.4770
6	195—225°	3%	0.9456	1.4790
7	Residue	trace	—	—

Isopulegol.

The first fraction was ascertained to be composed mostly of isopulegol which was isolated by fractional distillation, showing the constants:

B.p. 100°–102,° 22 mm.; $d_4^{20}=0.9077$; $n_D^{20}=1.4690$; $[\alpha]_D=+3°\ 26'$

Menthoglycol.

The third fraction which was assumed to be composed of glycol on dividing by distillation into the three portions gave the following figures:

	Fraction	Yield	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	145°—146° 15mm.	10%	0.9772	1.4714	$+7°\ 30'$
2	146°—151° "	45 "	0.9771	1.4710	$+3°\ 17'$
3	151°—152° "	45 "	0.9748	1.4710	±0

An Ethereal Compound.

The fifth fraction which was distilled on metallic sodium under 20 mm. pressure, shows B.p. 191.°5 at 16 mm.; $d_4^{20}=0.9341$; $n_D^{20}=1.4760$; $[\alpha]_D=-5.°30'$.

It was analysed with the following results:

0,1110 grm. gave 0.3194 grm. CO_2 and 0.118 grm. H_2O, C=78.5; H=11.9; theory requires C=77.9; H=11.7 for $C_{20}H_{36}O_2$. or C=78.4; H=11.1 for $C_{20}H_{34}O_2$.

It yields neither phenyl urethane nor any oxime, and was reduced by means of hydrogen and platinum black to a hydrogenated compound:

$d_4^{20}=0.9155$; $n_D^{20}=1.4635$; $[\alpha]_D=-2°52'$.

M.R.=93.4, theory 93.4 for $C_{20}H_{38}O_2$.

3. Action of 50% Sulphuric Acid on Citronellal.

The reaction product formed by the interaction between citronelall & 50% sulphuric acid under conditions similar to the above cases, was fractionated under 14 mm. pressure into 5 fractions:

	Fraction	Yield
1	60°— 90°	14%
2	90°—130°	1 "
3	130°—175°	1 "
4	175°—195°	62 "
5	195°—205°	17 "
6	Residue	5 "

Citronellal-terpene, $C_{10}H_{16}$.

The first fraction which differs from isopulegol in its physical & chemical characters, was analysed after distilling on metallic sodium:

	Fraction	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	173°—177°	0.8434	1.4840	+33° 30′
2	177°—181°	0.8506	1.4915	+36° 54′
3	181°—185°	0.8637	1.4980	+49° 11′

0.1054 grm. gave 0.3413 grm. CO_2 & 0.1093 grm. H_2O, C=88.3; H=11.5; theory C=88,2; H=11.8 for $C_{10}H_{16}$

The physial cconstants $d_4^{20}=0.8535$; $n_D^{25}=1.4875$; M. R.=45.9, agree well with those of monocyclic terpene with two double bonds in its molecule, and was named citronellal-terpene by the writer on account of its properties which gave neither hydrochloride nor nitross chloride and do not agree with those of known terpenes in the literature

Ethereal Compound, $C_{20}H_{36}O_2$.

The two fractions, B.p. (175°–195°) 14 mm. & B.p. (195°–205°) 14 mm. combined together and distilled again and divided into 3 fractions:

	Fraction	d_4^{20}	n_D^{20}	$[\alpha]$
1	196°—198° 19mm.	0.9295	1.4805	—5° 48′
2	198°—199. "	0.9262	1.4800	—2° 5′
3	201° 23mm.	0.9312	1.4820	—9° 3′

It was indicated in the above physical constants indicate that these fractions would be a mixture of a principal constituent and some others differing in their proportions, and also that the main constituent to each fraction was ascertained from the analysis, to be an ethereal compound and the chemical nature of the first fraction:

0.1319 grm. gave 0.3806 grm. CO_2 and 0.1386 grm, H_2O, C=78.7; H=11.7; theory requires C=78.8; H= 11.7 for $C_{20}H_{36}O_2$.

4. Action of Potassium Hydrogen Sulphate on Citronellal.

Citronellal was heated with twice its weight of powdered potassium hydrogen sulphate on an oil bath, when the temperature of the bath had reached 140,° a violent reaction took place, separating a water layer, and the reaction product washed with water and then subjected to fractional distillation proved to be:

	Fraction	Yield	d_4^{20}	n_D^{20}
1	—90° 15mm.	3%	0.8840	1.4670
2	90°—92. "	3 "	0.9035	1.4714
3	92°—92.5° "	5 "	0.9104	1.4720
4	92.5°—100° "	1 "	0.9137	1.4726
5	100°—130° "	1 "	0.9190	1.4730
6	130°—180° "	0.5 "	0.9212	1.4775
7	180°—190° "	3 "	0.9162	1.4840
8	190°—191° "	1.5 "	0.9150	1.4832
9	191°—193° "	64 "	0.9137	1.4837
10	193°—195° "	8.5 "	0.9171	1.4841

	Fraction	Yield	d_4^{20}	n_D^{20}
11	195°—197° "	4.5 %	0.9202	1.4852
12	Residue	5 "	—	—

Isopulegol.

Second and third fractions combined together and distilled again and the fraction B.p. 92°—92.5° at 15 mm.; $d_4^{20}=0.9105$; $n_D^{20}=1.4720$; $[\alpha]_D=+6°\ 10'$, was confirmed to be composed of isopulegol by oxidizing it into isopulegone which yields an oxime with m.p. 121.°

Di-isopulegol Ether, $C_{20}H_{34}O$.

Two fractions, B.p. 191°—193°; B.p. 193°—195°, combined together and distilled, and the fraction B.p. (185°) 12.5 mm. pressure, shows:

$d_4^{20}=0.9120$; $n_D^{20}=1.4835$; $[\alpha]_D=12°\ 15'$, and on analysis. 0.1205 grm. gave 0.3642 grm. CO_2 and 0.1271 grm. H_2O,; C=82.4; H=11.7, theory C=82.9; H=11.7 for $C_{20}H_{34}O$.

It gave no phenyl urethane, oximes or semicarbazide, and 1 gm. of the substance absorbed 162 cc. of hydrogen in presence of platinum black. Molemular refractive power of the substance being 90.0, agrees with the theoretical value 90.9 which was calculated for the molecular formula $C_{20}H_{34}O$ containing two double bonds in the molecule.

The physical constants of the reduced compound was determined to be:

$d_4^{20}=0.8932$; $n_D^{20}=1.4678$; $[\alpha]_D=+6°\ 1'$

M.R.=91.5: theory 91.8 for $C_{20}H_{34}O$.

5. Action of Acetic Anhydride & Sodium Acetate on Citronellal.

In order to learn the behavior of the aldehydes toward acetic anhydride and sodium acetate, a mixture of acetic anhydride and sodium acetate was heated with citronellal on an oil-bath at 150° for 15 hours, according to the directions put forward by F. Tiemann & R. Schmidt.[1] The reaction product which shows the ester value 316.0, was fractionated:

1 Ber. D. Chem. Ges., **29**, 913 (1896); and refer: F.W. Semmler: Ibid **42**, 2015 (1909).

	Fraction	Yield	d_4^{20}	n_D^{20}	$[\alpha]_D$	E.V.
1	106°—110° 12.5mm	20%	0.9200	1.4566	— 37′	288.2
2	112°—116° "	65 "	0.9082	1.4572	—4° 30′	300.6
3	116°—120° "	34 "	0.9054	1.4582	—7° 9′	302.9
4	147.5°—150.5° "	30 "	0.9747	1.4460	+1° 14′	439.5

It was ascertained from their physical constants and ester values (E.V) that the first, third and forth fractions were composed of isopulegol acetate, enol monoacetate of citronellal, and enol diacetate of citronellal respectively, and the second fraction was assumed to be a mixture of isopulegol acetate and enol acetate of citronellal.

6. Action of Acetic Anhydride on Citronellal.

Citronellal was heated with acetic anhyeride on an oil-bath at 150°, for 15 hours, and the reaction product, treated with hydrogen sodium sulphite to remove an unchanged aldehyde, and remaining oil showed:

$d_4^{20}=0.8504$; $n_D^{20}=1.4490$; $\alpha_D=+10°.35'$ and ester value 323, was subjected to fractional distillation:

	Fraction	Yield
1	90°—100° 9mm.	13%
2	100°—105° "	46 "
3	105°—110° "	6 "
4	110°—140° "	7 "
5	140°—150° "	20 "
6	150°—160° "	4 "
7	Residue	4 "

The main fractions (1,2 and 5) by further distillation under 12.5 mm. pressure, were divided into the two portions with the following constants:

	Fraction	d_4^{20}	n_D^{20}	$[\alpha]_D$	E.V.
1	102°—106°	0.9396	1.4590	—1° 45′	284
2	147.°5—150.°5	0.9780	1.4475	+2° 36′	—

Isopulegol Acetate.

The first fraction was assumed to be composed of isopulegol acetate

from its physical constants and ester value. In confirmation the free alcohol was isolated by saponification of the ester, which was found to be possessed of the following properties B.p. 92.5°—93.5° at 14 mm. $d_4^{20}=0.9150$; $n_D^{20}=1.4723$; $[\alpha]_D=+4°\ 10'$ and these constants agree well with those of isopulegol.

7. Action of Glacial Acetic Acid on Citronellal.

By the interaction of citronellal and glacial acetic acid at 150° for 15 hours, isopulegol and its acetate were obtained from the reaction product which was fractionated after being separated from the unchanged citronellal.

	Fraction	Yield
1	65°—100° 16mm.	5%
2	100°—110° 〃	46 〃
3	110°—151° 〃	6 〃
4	151°—181° 〃	6 〃
5	181°—203° 〃	37 〃

The first two fractions B.p. 65°—100°, B.p. 100°—110,° by repeating the distillation were divided into two portions:

	Fraction	d_4^{20}	n_D^{20}	$[\alpha]_D$	E.V.
1	100°—105° 15.5mm,	0.9254	1.4617	$+1°\ 40'$	180
2	105°—110° 〃	0.9367	1.4586	$-1°\ 10'$	260

The two fractions when hydrolysed yielded equally isopulegol B.p. (100°—101°) 20mm. $d_4^{20}=0.9143$ $n_D^{20}=1.4720$; $[\alpha]_D=+4°\ 41'$ and also yielded by further acetylation with acetic anhydride & sodium acetate isopulegol acetate B.p. (94°—97°) 8mm. $d_4^{20}=0.9394$; $n_D^{20}=1.4572$ $[\alpha]_D=-1°\ 10'$.

From the other fractions no definite compound could be obtained by distillation.

II. Citral.

8. Action of 5% Sulphuric Acid on Citral.

The citral used in the experiment was obtained from the East

Indian lemon-grass oil by distillation and was purified by the sulphite method.

B.p. 112.5°—115° at 17mm pressure, $d_4^{20}=0.8886$; $n_D^{20}=1.4901$; $[a]_D=0°\ 10'$.

It was treated according to the directions suggested by F. Tiemann[1], with 10 times the quantity of 5% sulphuric acid at 27° for 12 hours. The product estimated to contain 86% free citral by the sulphite method, was fractionated under 20 mm. pressure after the unchanged citral had been removed.

	Fraction	Yield	d_4^{20}	n_D^{20}
1	to 100°	1.5	0.9723	1.4995
2	100°—115°	6.5	0.9320	1.4950
3	115°—118°	73	0.9085	1.4914
4	118°—140°	4.5	0.9214	1.4920
5	Residue	14.5	—	—

The third fraction by repeated fractional distillation shows the constants: $d_4^{20}=0.9080$; $n_D^{20}=1.4902$; $a_D=\pm 0$ which differ from those of citral. However; it yields *a*-citryl-*β*-naphthio-cincomenic acid with a melting point of 197.°

9. Action of 20% Sulphuric Acid on Citral.

By the interaction of citral with 10 times the quantum of 20% sulphuric acid at 25° for 12 hours, besides resinous substance, some cyclic terpenes were obtained. The product was fractionated under 22 mm. pressure:

	Fraction	Yield
1	to 80°	23%
2	80°—100°	10 〃
3	100°—196°	5 〃
4	196°—199°	27 〃
5	Residue	35 〃

1 Ber. D. Chem. Ges., **32**, 114 (1899).

The first and second fractions combined together and subjected to distillation over metallic sodium under ordinary pressure; and the fraction, B.p. 183°–186°, $d_4^{20}=0.8886$; $n_D^{20}=1.5092$, was analysed with the following results:

0.1187 grm, gave 0.3883 grm. CO_2 and 0.1115 grm. H_2O,
C=89.2; H=10.5; theory requires C=89.5; H=10.5 for $C_{10}H_{14}$.

Chemical properties and physical constants M.R. = 45.1, theory requires 44.8 for $C_{10}H_{14}F_3$, of the fraction indicates the occurrence of a new terpene in it, which was named by the writer citral terpene.

The third & fourth fractions show the occurrence of a compound of unstable nature toward heat since the fractions by repeated distillations abundantly yielded resinous matter with the boiling point ranging from 150° to 200° under 14 mm. pressure, and the main portion B.p. 194°—199° 17 mm.; $d_4^{20}=0.9494$: $n_D^{20}=1.5303$; $\alpha_D=-0.4°$; 0,1256 grm. subst. gave 0.4003 grm. CO_2 and 0.1185 grm. H_2O, C=86.7; H=10.5 which shows an unsaturated nature towards chemicals, and was assumed to be a mixture of diterpene and a compound of ethereal nature.

10. Action of 50% Sulphuric Acid on Citral.

Citral by the action of 50% sulphuric acid at 20°, was converted into a resinous substance, cymene, and substances of unknown nature. For the isolation of these compounds, the reaction product was distilled under 20 mm. pressure.

	Fraction	Yield
1	70°— 90°	6%
2	90°—100°	25 〃
3	100°—198°	5 〃
4	198°—220°	14 〃
5	Residue	50 〃

The second fraction by distillation over metallic sodium yielded a fraction with a B.p. 174.5°–175°, $d_4^{20}=0.8588$; $n_D^{20}=1.4892$, which was mostly composed of p-cymene.

The fourth fraction was assumed to be composed mostly of the portion of the properties B.p. (189°–193°) 16mm. $d_4^{20}=0.9616$;

n_D^{20} 1.5303; 0.1108 grm. gave 0.3512 grm. CO_2 & 0.1042 grm. H_2O, C=86.5; H=10.5;

11. Action of Potassium Hydrogen Sulphate on Citral.

By the action of potassium hydrogen sulphate on citral at 140° for 30 minutes, p-cymene and a diterpene were obtained from the reaction product which was subjected to fractional distillation under 14 mm. pressure after the usual treatment.

	Fraction	Yield
1	to 70°	35%
2	70°—100°	7 〃
3	100°—180°	5 〃
4	180°—192°	14 〃
5	192°—201°	9 〃
6	Residue	30 〃

p-Cymene was isolated from the first and second fractions by distillation over metallic sodium, B.p. 174°-175°, d_4^{20}=0.8572; n_D^{20}= 1.4678.

For confirmation, it was oxidized to p-oxyisopropyl-benzoic acid of m.p. 155°—157°.

Other fraction by repeated fractional distillations were found to consist mostly of hydrocarbon of the formula $C_{20}H_{28}$, which shows the following constants; B.p.=(190°-194°) 14mm.; d_4^{20}=0.9244; n_D^{20} = 1.5280; 0.1493 grm. subst. gave 0.4872 grm. CO_2 & 0.1412 grm. H_2O, C= 89.0; H=10.6.

By reduction with hydrogen and platinum black, 1 gm. of substance absorbs 258 c.c. hydrogen, and the resulting compound; d_4^{20} = 0.8840; n_D^{20}=1.4875 shows a still unsaturated nature toward an iodine solution.

12. Action of Acetic Anhydride on Citral.

When citral came into contact with acetic anhydride at 23°, no reaction could be observed, but when the temperature was raised to 150°, a reaction took place in the formation of a product which was separated

from the unchanged citral (14%) by the sulphite method, and distilled under 19 mm. pressure:

	Fraction	Yield	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	to 100°	4%	0.8805	1.4889	—
2	100°—120°	5 〃	0.9340	1.4860	—
3	120°—125°	8 〃	0.9650	1.4890	—
4	125°—127°	10 〃	0.9520	1.4830	—
5	127°—132°	20 〃	0.9520	1.4860	—0° 27′
6	132°—135°	8 〃	0.9558	1.4905	—
7	135°—140°	6 〃	0.9598	1.4909	—
8	Residue	40 〃	—	—	—

Enol Citral Acetate.

The fourth and fifth fractions were assumed from then physical constants to be equally composed of enol citral acetate, and the analytical results confirm this assumption.

0.1467 grm. gave 0.3959 grm. CO_2 & 0.1270 grm. H_2O,
C=73·6; H=9.6 theory requires
C=74·2; H=9·3 for $C_{12}H_{18}O_2$.

13. Action of Glacial Acetic Acid on Citral.

By the action of glacial acetic acid on citral at 150° for 15 hours, p-cymene could be isolated from the reaction product of an ester value of 44.4, which on distillation gave the following results:

	Fraction		Yield
1	60°—100°	16 mm.	33%
2	100°—130°	〃	3 〃
3	130°—190°	〃	6 〃
4	190°—200°	〃	18 〃
5	200°—203°	〃	5 〃
6	Residue	〃	—

Cymene was composed of the first fraction, which, isolated by distillation under ordinary pressure, gave the constants:

B.p. 174°–174.5°; $d_4^{20}=0{\cdot}8571$; $n_D^{20}=1.4942$.

III. Isopulegol.

14. Action of 20% & 50% Sulphuric Acid on Isopulegol.

Isopulegol which was isolated from isopulegol acetate by hydrolysis gave the constants:

B.p. 100.9°–101°, 20mm., $d_4^{20}=0.9143$; $n_D^{20}=1.4720$; $[\alpha]_D=+4°\ 41'$.

It was treated with 10 times by weight of 20% sulphuric acid at 15° for 12 hours, and the product was treated as usual.

	Fraction	Yield	d_4^{20}	n_D^{20}	$[\alpha]_D$
1	86°— 89°/10mm.	87%	0.9151	1.4714	+3° 8′
2	89°— 92° 〃	44〃	0.9177	1.4712	+2° 57′
3	92°—100° 〃	7〃	—	—	
4	100°—135° 〃	5〃	—	—	
5	135°—140° 〃	2〃	—	—	
6	140°—142° 〃	5〃	0.9640	1.4720	
7	Residue	trace	—		

By this treatment the main part of the isopulegol remained without any reaction from the sulphuric acid and some part was converted into menthoglycol by adding a water molecule, and the latter substance was isolated from the sixth fraction.

When, however, isopulegol was treated with 50% sulphuric acid at 17°C, for 13 hours, a terpene of a nature identical with that of the citronellal terpene above mentioned, and a substance of ethereal nature were isolated from the product by fractional distillation.

	Fraction	Yield	d_4^{20}	d_D^{20}	$[\alpha]^D$	Remark
1	to 86° 13mm.	22%	0.8582	1·4890	—	Terpene
2	86°—140° 〃	10〃				
3	140°—170° 〃	13〃				
4	170°—185° 〃	10〃				
5	185°—190° 〃	36〃	0.9471	1.5011	—8° 9′	Ethereal
6	Residue 〃	9〃	—	—	—	compound

15. Action of Potassium Acid Sulphate on Isopulegol.

Isopulegol was treated with potassim hydrogen sulphate under the

same conditions described in the case of citronellal, and the reaction product was distilled under 14.5 mm. pressure, and di-isopulegol ether, which was previously prepared by Verley[1] was isolated as shown in the following table.

	Fraction	Yield	d_4^{20}	n_D^{20}	$[\alpha]_D$	Remark
1	80°— 90°	13%	—	—	—	Isopulegol
2	90°—110°	14 〃	—			—
3	110°—189°	3 〃	—			—
4	189°—193°	60 〃	0.9110	1.4861	+3° 3′	Ether
5	Residue	10 〃				

When the ether reduced with hydrogen and platinum black, yielded a compound with the following properties $d_4^{20}=0.8868$, $n_D^{20}=1.4666$; $[\alpha]_D=+24°29'$.

IV. Menthoglycol.

16. Action of Sulphuric Acid on Methoglycol.

The menthoglycol used in this experiment shows the constants: B.p. (141°–146°) 13 mm. $d_4^{20}=0.9806$; $n_D^{20}=1.4730$ $[\alpha]_D=+6°\ 31'$.

When menthoglycol was subjected to the action of 20% sulphuric acid at 12° for 12 hours, the main part (80%) of the substance remained in an unchanged state. (B.p. 140°–147°, 13mm., $d_4^{20}=0.9784$; $n_D^{20}=1.4720$; $[\alpha]_D=+8°\ 22'$.)

By the action of 50% sulphuric acid on menthoglycol at 12°, it was transformed partly into the so-called citronellal terpene (with the following properties, B.p. 175°–181°, $d_4^{20}=0.8583$; $n_D^{20}=1.4900$) which was isolated from the first fraction of the reaction product by distillation.

	Fraction		Yield	d_4^{20}	n_D^{20}
1	to 95°	10 mm.	44%	—	—
2	95°—170°	〃	trace	—	—
3	170°—180°	〃	22 〃	0.0355	1.5125
4	180°—190°	〃	18 〃	0.9430	1.5130
5	Residue	〃	16 〃	—	—

1 Loc. Cit.,

17. Action of Potassium Hydrogen Sulphate on Menthoglycol.

By the interaction of the glycol and potassium hydrogen sulphate, the so-called citronellal-terpene and di-isopulegol ether were isolated from the reaction product by distillation under 15–16 mm. pressure.

	Fraction	Yield	d_4^{29}	n_D^{20}	Remark
1	74°— 79°	13%	0.8713	1.4930	Terpene
2	79°— 84°	9 〃	0.8810	1.4911	—
3	84°—192°	18 〃	—		
4	192°—193°	40 〃	0.9140	1.4855	Ether
4	193°—196°	13 〃	0.9137	1.4867	—
5	Residue	7 〃	—	—	—

V. Menthol.

18. Reduction of Isopulegol., and Formation of l.-Menthol.

Isopulegol prepared from its acetate of B.p. (101·5°–104.5°) 12 mm, $d_4^{20}=0.9378$; $n_D^{20}=1.4570$; $a_D=-33'$, by saponification with alcoholic potash, boils at 91.5° under 13 mm. pressure, $d_4^{20}=0.9162$; $n_D^{20}=1.4710$; $a_D=-30'$.

When the alcohol was reduced with hydrogen in presence of platinum black in its glacial acetic acid, yields menthol of the following properties:

$d_4^{25}=0.8944$; $n_D^{25}=1.458$; $[a]_D=-16°$. 77 grm. of the sample were fractionated under 18 mm. pressure into 4 parts, and the fractions shows the following constants:

	Fraction	Yield	d_4^{25}	$[a]_D$
1	87°—100°	2.3 grm.	0.8772	− 9°.80
2	101°—103°	16·0 〃	0.8922	−11°.77
3	104°—106°	45.0 〃	0.8931	−18°.25
4	107°—108°	7.5 〃	—	−26°.75
5	Loss	6. 〃	—	—

The fourth faction solidified on cooling and the crystals separated were found to melt at 30°. By further distillation of the third fraction, the fraction which regarded to consist mostly of menthol was isolated.

Laevo Menthol.

The third fraction in the above table was further fractionated under 15 m.m. pressure and two fractions were resulted:

	Fraction	Yield	d_4^{25}	$[\alpha]_D$
1	102°—103°	15.2 grm.	0.8924	—13.°22
2	105°—106°	28·3 〃	solid	—26.°06

The first fraction was then subdivided by distillation under 25 m.m. into 3 portions:

	Fraction	Yield	$[\alpha]_D$	Remark
1	108°—109°	8.3 grm.	—9.°58	liquid
2	109°—110°	4.2 〃	—16.°50	solid
3	110°—111°	3.0 〃	—23.°76	〃

The fractions which mentioned above and show the rotatory power–(23°~26°) combined together, and subjected to distillation in order to isolate pure l-menthol, and finally obtained a compound which possessed the physical constants, M.p. 33°—34°; $[\alpha]_D = -44,°92$, agree well with those of pure l-menthol.

Other fractions which show the low rotatory power, were treated, with phthalic anhydride following the direction by Pickard & Littlebury, and l-menthol hydrogen phthalate of M.p. 128°—131°; $[\alpha]_D = -32.°42$ in acetic acid solution, was isolated. Thus, the yield of l-menthol isolated in the free and combined states was amounted to be 26% of the reduction product from isopulegol.

Laevo Menthone.

Menthol obtained from isopulegol by catalytic reduction was oxidized with chromic acid following the directions suggested by E. Beckman[2] into menthone which was then converted into its oxime with the following constants: m p. 54°-62°; $[\alpha]_D = -43°.21$ The oxime was purified by converting it into hydrochloride in its ethereal solution, and by repeating the operation pure laevo menthone oxime hydrochloride was isolated as will be seen in the following table:

1 Loc. cit.,

2 Liebig Ann., **250**, 322 (1888).

	First crystallisation	Second "	Third "	Hiraidzumi's sample
m.p.	106°–107°	110°–112°	114°–116°	115°–116°
$[\alpha]_D$	−47°.78	−54°.65	−58°.77	−56°.21
$[\alpha]_{H\alpha}$	−42°.66	−41°.46	−47°.77	−47°.96
$[\alpha]_{H\beta}$	−67°.00	−75°.40	−75°.17	−84°.87
$[\alpha]_{462}$	−74°.23	−87°.45	−84°.96	−94°.30

Beckmann[1] has described M. p. 117°–118°; $[\alpha]_D = -62°$. for pure l-menthone oxime hydrochloride, while the pure sample prepared by Dr. T. Hiraidzumi shows the constants mentioned in the table.

In conclusion, the writer wishes to express his sincere thanks to Dr. T. Kainosho, Director of the Takasago Perfumery Co., for his encouragement in carrying out of this research and also to Professor S. Komatsu of Kyoto Imperial University under whose advice and suggestions this work was preformed.

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1 Ber. D. Chem. Ges., **42**, 846 (1909).

Bending of Aluminium-Crystals

By

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(Received April 18, 1928)

Abstract

The effect of bending upon the aluminium plates composed of large single crystals was investigated by means of distortions of the Laue-spots. The orientations of the micro-crystals, produced by the destruction of the single crystal at the time of bending, were found to be scattered around the axis of bending including the initial orientation, so that the micro-crystals revolve to some extent around this axis of bending, and finally their arrangement becomes fibrous by the process of bending. The same result was also obtained in the case of aluminium-wires each composed of a single crystal when they were subjected to a slight bending.

It is well known that when a metal crystal is subjected to various regular cold workings it is regularly destroyed by this process, and that finally the micro-crystals produced by the destruction of the crystal take a definite arrangement which is peculiar to the kind of working and that of the metal. In this paper is reported the results of an investigation with X-rays of the effects of bending upon the aluminium plates and wires each composed of a single crystal. The test-pieces of the plates measured 10 cm. × 2 cm. × 1.5 mm., and the diameter of the wires examined was 3 mm. The large single crystals were obtained by the stress-annealing method.

The orientations of the crystals in the plates were first determined by taking their Laue-photographs. These plates were then bent by being pressed against the surface of a circular cylinder, so as to have the same radius of curvature as the radius of the cylinder. Then they were bent more and more in succession by using circular cylinders of smaller radii, and finally they were folded into two without using any cylinder. At each stage of bending a Laue-photograph was taken by

letting the X-rays strike the specimen in the direction of the radius of curvature of the plate. In the photographs thus taken the sharp Laue-spots of the initial single crystal became more and more diffuse and lengthened nearly in the direction radial from the central spot as the process of bending proceeded. This phenomenon was also seen when the single crystal was subjected to other cold workings such as rolling, extension or tortion, and seems to be caused by the scattering of the orientations of the micro-crystals, which are produced by the destruction of the single crystal, for some angles around a certain axis of revolution

At the suggestion of Prof. U. Yoshida the writer tried to determine the axis of revolution of the micro-crystals in the case of bending; and he obtained the photographs shown in Figs. 1 and 2, Plate I, by using general X-rays from the tungsten anticathode. These figures are of two different specimens, and in both cases the radius of curvature of bending is 1.85 cm., and the horizontal direction in each figure is parallel to the axis of bending.

The axis of revolution around which the orientations of the micro-crystals are scattered was determined by the following consideration. The whole assemblage of the end-points, which represent the positions of both ends of every lengthened Laue-spot, must be two sets of ordinary Laue-spots due to the micro-crystals at two different orientations. Thus, if we can select, by taking either one of the two end-points of every lengthened Laue-spot respectively, one half of all the end-points above mentioned which constitute one set of ordinary Laue-spots due to the micro-crystals at a certain orientation; then, the remaining end-points will belong to another set of the ordinary Laue-spots due to the micro-crystals at another orientation rotated a little from the former. These two different orientations of the micro-crystals are two extreme ones, and the intermediate portion between the two extremities of every lengthened Laue-spot, will be caused by the micro-crystals at the intermediate orientations between the two extreme ones. By means of the globe and the spherical scale devised by Prof. U. Yoshida,[1] these two extreme orientations of the micro-crystals, and consequently the axis of their revolution were determined.

The writer determined the axis of revolution of the micro-crystals for many single crystals of aluminium of different orientations, and could

1 Jap. J. Phys., 4, 133 (1927)

find that this axis of revolution of the micro-crystals coincided always with the axis of bending irrespective of the orientation of the initial single crystal. This point was confirmed by the agreement of the photographs with the diagrams calculated under the above consideration. Figs. 1 and 2 are the calculated diagrams which correspond to Figs. 1 and 2, Plate I, respectively, and they are both drawn by taking 7° as the angle of revolution of the micro-crystals around the axis of bending. In these figures the dots indicate the positions of the initial Laue-spots.

Fig. 1

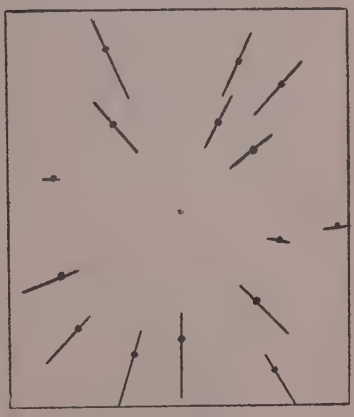

Fig. 2

The angle of revolution of the micro-crystals becomes larger with a smaller radius of curvature of the plate, and the arrangement of the micro-crystals approaches more to the fibrous one. Figs. 3 and 4 Plate I, are the photographs taken with the same plates as in Figs. 1 and 2 Plate I respectively, when they are folded into two, and show almost the same features as those of a fibrous arrangement of the micro-crystals. Fig. 3 shows, in stereographic projection, the initial orientations of these specimens I and II in reference to the crystallographic axes of the crystals; here the dot indiacates the direction of the axis of bending or the common axis of the fibrous arrangement, and the small circle the direction lying in the plane of the plate and perpendicular to the axis of bending. Fig. 4 and Eig. 5 are the diagrams, for the Laue-photographs Fig. 3 and Fig. 4, Plate I, respectively, calculated by taking 90°

equally on both sides of the initial orientation as the angle of revolution

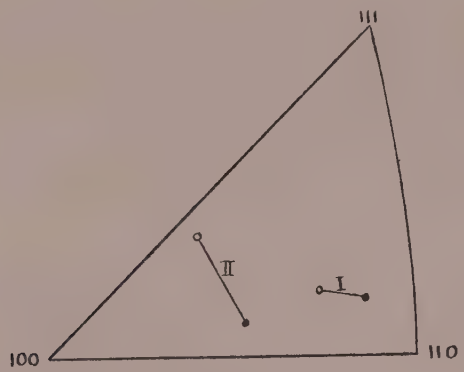

Fig. 3

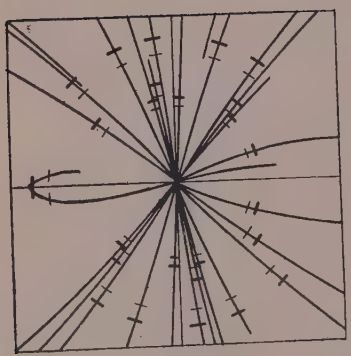

Fig. 4

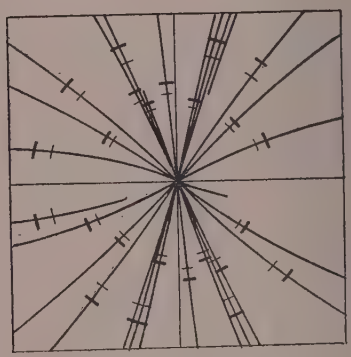

Fig. 5

of the micro-crystals around the axis of bending; and they show a close agreement with Fig. 3 and Fig. 4, Plate I, respectively.

Thus we can obtain merely by bending the fibrous arrangement of the micro-crystals, which has any crystallographic axis in the direction parallel to the axis of bending, as the axis of the fiber. This seems not to be without interest, because with some regular cold workings, some particular crystallographic axes become always the axis of the fiber.

To see whether the same result as the above one can be obtained in the case of aluminium wires each composed of a single crystal, the writer examined the wire, subjected to a slight bending at a small portion of it, by illuminating the wire with divergent X-rays passing through a narrow and long slit.[1] In this case the bending of the wire was so small that the distance between the bent portion of the wire and the photographic plate could be regarded as unaltered by the bending. One of the photographs thus taken is shown in Fig. 5, Plate I. We can see from the difference of the distortions of the diffraction-lines that the effect of bending upon various reflecting atomic planes of the crystal differ with the orientation of the atomic planes. By determining the orientations of various reflecting atomic planes, to which are due the diffraction-lines appearing in several photographs taken at different orientations of the wire, it was ascertained that the smaller the angle between the normal of the reflecting atomic plane and the axis of bending, the smaller the distortion of the diffraction-line which is caused by the atomic plane. This shows that, in the case of the wire, we have also the same scattering of the orientations of the micro-crystals as in the case of the plate.

In conclusion, the writer wishes to express his sincere thanks to Prof. U. Yoshida for his kind guidance in the research.

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1 Nature, **118**, 912 (1926)

Fig. 1

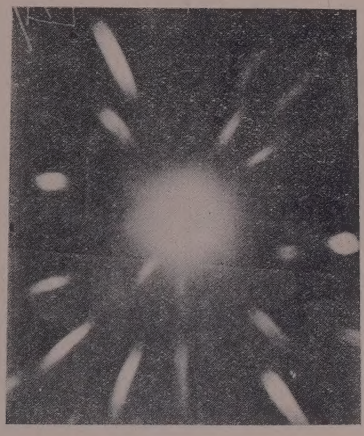

Fig. 2

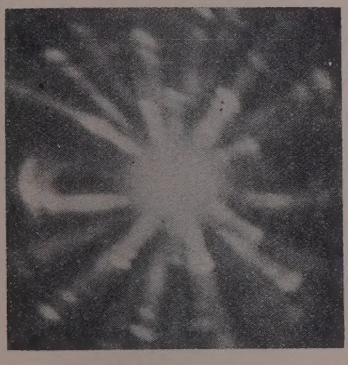

Fig. 3

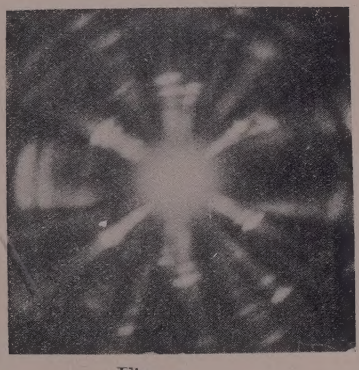

Fig. 4

Fig. 5

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